Volume

1

ENVIRONMENTAL RESEARCH

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LES RECHERCHES SUR L'ENVIRONNEMENT

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PROCEEDINGS

VOLUME I:

KEYNOTE PRESENTATIONS
FEATURE PRESENTATIONS
PANEL PRESENTATIONS
AIR QUALITY RESEARCH
WATER QUALITY RESEARCH

THE CHALLENGES OF A NEW DECADE

November 19 & 20, 1990
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Sponsored by

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Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1990 Technology Transfer Conference are published in two volumes of conference Proceedings corresponding to the following sessions:

VOLUME I:	KEYNOTE PRESENTATIONS FEATURE PRESENTATIONS PANEL PRESENTATIONS AIR QUALITY RESEARCH WATER QUALITY RESEARCH
VOLUME II:	KEYNOTE PRESENTATIONS FEATURE PRESENTATIONS PANEL PRESENTATIONS LIQUID & SOLID WASTE RESEARCH ANALYTICAL METHODS ENVIRONMENTAL SOCIO-ECONOMICS MULTIMEDIA CONTAMINANTS & BIOTECHNOLOGY

Volume I is comprised of presentations given during Session A and Session B of the conference, as well as all Keynote, Feature, and Panel Presentations.

For reference purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573

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VOLUME I

INDEX

Keynote Presenters **Page**

Sustainable Development: The Technological Challenge; Noel J. Brown, Director, United Nations Environment Programme 1

Responses to Global Climate Change: The Coming Environmental and Economic Revolutions; Jim Bruce, Chair, Canadian Climate Program Board 2

Feature Presenters

Air Quality Research

A1 **What's the Latest on Acidic Deposition in North America?;** D. Sisterson, Argonne National Laboratory, Argonne, Illinois, USA 5

A10 **Measurement of Semi-Volatile Organic Compounds in Ambient Air;** G. Hunt, ENSR, Acton, Massachusetts, USA 7

Water Quality Research

B1 **Influence of the Zebra Mussel *(Dreissena polymorpha)* on Water Quality of Lake Erie;** J. Leach, Ontario Ministry of Natural Resources, Wheatley, Ontario 8

B10 **Cross-Disciplinary Analyses of Environmental Health Studies Suggest the Need for New Approaches to Risk Assessment;** T. Colborn, US Conservation Foundation, Washington D.C., USA 10

Volume I **Page**

Liquid & Solid Waste Research

C1 **Environmental Concerns - Keeping our Perspective;** J.P. Nunan, Trow, Dames & Moore, Mississauga, Ontario 12

C10 **Oxidation to Remove Trichloroethylene from Soil;** G. Farquhar, University of Waterloo, Waterloo, Ontario 16

Analytical Methods Research

D1 **Ion Mobility Spectrometry in Atmospheric Environmental Monitoring in the U.S. Space Program;** G.A. Eiceman, New Mexico State University, Las Cruces, New Mexico 17

Environmental Socio-Economics

E1 **Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market;** B. Hull, The Conference Board of Canada, Ottawa, Ontario 19

Multimedia Contaminants & Biotechnology

F1 **Utilization of Environmental Research to Control Lead Contamination;** B.G. Wixson, Clemson University, Clemson, South Carolina, USA 20

Panel Presentations

Global Warming: What is at Stake?

P1 **The International Scene;** J.P. Bruce, Chair, Canadian Climate Program Board 26

P2 **Global Warming: A Canadian Perspective and Action Strategy;** D.K. Dawson, Director General, Canadian Climate Centre 27

Volume I Page

P3 **Global Warming: What is at Stake? Socio-Economics;** E. Haites, Barakat & Chamberlin Inc. 28

P4 **Warming to a Crisis: The Media and Climate Change;** M. Keating, Environmental Writer 32

P5 J.D. McFarland, Imperial Oil Limited 36

P6 **Global Warming: What's Known and What's Not?;** B. Yang, Ontario Cabinet Office 37

VOLUME I

SESSION A: AIR QUALITY RESEARCH

Verbal Presentations **Page**

A2 **Genetic Characteristics of Healthy and Declining Sugar Maple *(Acer saccharum Marsh)* in Ontario;** P. Knowles, Lakehead University, Thunder Bay, Ontario 38

A3 **Interpretation of Sugar Maple *(Acer saccharum)* Ring Chronologies from Central and Southern Ontario using a Mixed Linear Model;** D.A.J. Ryan*, O.B. Allen and A.M. Gordon, University of Guelph, Guelph, Ontario 46

A4 **A Method to Establish Background Concentrations of Contaminants and Nutrients in Soil and Vegetation;** R. Jones, Air Resources Branch, Environment Ontario, Toronto, Ontario 53

A5 **Further Developments in the Analysis of Three Dimensional Environmental Data;** P.K. Hopke* and Y. Zeng, Clarkson University, Potsdam, New York, USA 67

A6 **Evaluating the Comprehensive Model ADOM;** C. Fung*, R. Bloxam, P.K. Misra and S. Wong, Air Resources Branch, Environment Ontario, Toronto, Ontario 80

A7 **Modeling the Influence of Topography on Dense Gas Dispersion;** S.R. Ramsay* and R.E. Britter, EnviroTech Research Limited, London, Ontario 88

Volume I Page

A8 **Ignition Studies of Selected Explosive Mixtures of Gases and Dusts Emitted from Cement Kilns;** I.I. Inculet*, E.J. Weckman, G.S.P. Castle, K.A. Shelstad and M.L. Wick, The University of Western Ontario, London, Ontario 99

A9 **Evaluation of Methods to Determine the Impacts of Residential Woodburning on Ambient Air in Ontario;** M.E. Yandle*, C.S. Davis and D.L.M. Dougherty, Concord Scientific Corporation, Downsview, Ontario 104

A11 **A Study of the Peak Ozone Levels in the Toronto Area;** J.D. Smith* and L. Shenfeld, The MEP Co., Markham, Ontario 118

A12 **Developments of Monitoring Methods for Odorous Organics in Ambient Air;** C. Chan*, P. Forsythe, L. Vainer and J.W. Martin, Mann Testing Laboratories, Mississauga, Ontario 128

A13 **Atmospheric Measurements of Natural Hydrocarbons Using Gas Chromatography/Mass Spectrometry;** H. Niki* and B.H. Khouw, York University, North York, Ontario 136

A14 **Atmospheric Trace Gas Measurements Using a Tunable Diode Laser Absorption Spectrometer;** H.I. Schiff*, R. Berman, D.R. Hastie and S. Sharma, York University, North York, Ontario 149

Volume I Page

A15 **Uptake and Distribution of Naphthalene in Vegetable Plants Following Foliar and Root Exposure;** B. Hale-Marie* and D.P. Ormrod, University of Guelph, Guelph, Ontario 157

A16 **Phytotoxicity of Uranium;** S.C. Sheppard*, W.G. Evenden and A.J. Anderson, AECL Research, Pinawa, Manitoba 165

VOLUME I

SESSION A: AIR QUALITY RESEARCH

Poster Presentations		Page
AP1	**Identification of Odours. The Challenge of the Nineties;** A.C. Ng and G.B. De Brou, Air Resources Branch, Environment Ontario, Toronto, Ontario	173
AP2	**CO_2 Production and Carbon Cycling in Precambrian Shield Watersheds;** R. Aravena and S.L. Schiff, University of Waterloo, Waterloo, Ontario	177
AP3	**Modelling the Long Range Transport, Transformation and Deposition of Mercury;** R. Bloxam, S. Wong and P.K. Misra, Air Resources Branch, Environment Ontario, Rexdale, Ontario, E. Voldner and W. Schroeder, Atmospheric Environment Service, Environment Canada, G. Petersen, GKSS Research Centre, Germany	181
AP4	**An Investigation of Vibration Isolation in a House for Reduction of Train Vibration;** G. Pernica and J.H. Rainer, National Research Council Canada, Ottawa, Ontario	189
AP5	**Simultaneous Real Time Detection of Mercury and Hydrogen Chloride in Ambient Air;** M.D. Corbridge, G.B. DeBrou, A. Ng and N.S. Karellas, Air Resources Branch, Environment Ontario, Toronto, Ontario	192

Volume I Page

AP6 **A Residence Time Analysis of Air Data from the Acidic Precipitation in Ontario Study (APIOS);** N.W. Reid, A.J.S. Tang, M. Lusis and D. Yap, Air Resources Branch, Environment Ontario, Toronto, Ontario 196

AP7 **Microwave Induced Catalytic Decomposition of Some Gaseous Air Pollutants;** M.C. Depew, T. Dineson, M.Y. Tse and J.K.S. Wan, Queen's University, Kingston, Ontario 200

AP8 **Mesoscale and Long Range Transport Models are Combined to Model Pollutants Originating from Local and Distant Sources;** M. Niewiadomski, The MEP Company, Markham, Ontario 206

AP9 **Relationship of Sugar Maple Decline and Corresponding Chemical Changes in Sap Carbohydrates and Trace Elements;** D.N. Roy, S. Pathak, H.K. Mohamed and T.C. Hutchinson, University of Toronto, Toronto, Ontario 210

AP10 **Modelling Concentration Fluctuations;** E. Alp and A. Ciccone, Concord Scientific Corporation, Downsview, Ontario and C.S. Fung, Environment Ontario, Toronto, Ontario 214

VOLUME I

SESSION B: WATER QUALITY RESEARCH

Verbal Presentations **Page**

B2 **Early Biological and Life History Attributes of the Zebra Mussel, *Dreissena polymorpha* (Bivalvia: Dreissenidae), and Impacts on Native Bivalves in Lake St. Clair;** G.L. Mackie, University of Guelph, Guelph, Ontario 215

B3 **Toxicokinetic Modelling of Mixtures of Organic Chemicals;** L.S. McCarty*, G.W. Ozburn and A.D. Smith, Lakehead University, Thunder Bay, Ontario and D.G. Dixon, University of Waterloo, Waterloo, Ontario 232

B4 **Verification of a Bioconcentration-Based Model for Predicting Pulse-Exposure Toxicity of Organic Contaminants to Fish;** B.E. Hickie* and D.G. Dixon, University of Waterloo, Waterloo, Ontario 242

B5 **Mapping Lake Water Quality Characteristics Using Landsat Thematic Mapper Data;** J.R. Pitblado*, T.L.M. Jetty, R.L. O'Daiskey and D.A. Dempsey, Laurentian University, Sudbury, Ontario 250

B6 **Multispectral Remote Sensing Techniques for Past, Present and Future Mapping of Chlorophyll;** A.R. Kalinauskas*, Moniteq Ltd, Concord, Ontario, N.J. Hutchinson and B.P. Neary, Dorset Research Centre, Environment Ontario, Dorset, Ontario 256

Volume I

Page

B7 **Regional Analysis of Low Flow Characteristics for Central and Southeastern Regions;** H.S. Belore*, D.A. Ashfield and S.P. Singh, Cumming Cockburn Limited, Willowdale, Ontario 258

B8 **Retractable Composite Absorbents for Environmental Clean-Up;** B. Gillies* and H. Auksi, Eco Corporation, Willowdale, Ontario and O. Meresz, Laboratory Services Branch, Environment Ontario, Toronto, Ontario 270

B9 **Advanced Technology for Destruction of Organic Pollutants in Water Streams;** H. Al-Ekabi*, A. Safarzadeh-Amiri, J. Story, W. Holden and G. Edwards, Nulite, a Division of Nutech Energy Systems Inc., London, Ontario 275

B11 **Carcinogenicity Testing of Bleached Kraft Mill Effluent Using *In-vivo* Rainbow Trout Assays;** C.D. Metcalfe*, M.E. Nanni and N.M. Scully, Trent University, Peterborough, Ontario 287

B12 **Impact of Bleached Kraft Mill Effluent (BKME) on Fish Populations Near Terrace Bay, Ontario;** M.E. McMaster* and D.G. Dixon, University of Waterloo, K.R. Munkittrick, Great Lakes Fisheries, C. Portt, C. Portt and Associates, G.J. Van der Kraak, University of Guelph, I.R. Smith and D. Rokosh, Environment Ontario 295

Volume I **Page**

B13 **Involvement of Bile Duct Disease and Loss of Resistance to Chemical Carcinogens in the Pathogenesis of Liver Neoplasms in Benthic Fish from Lake Ontario;** G.M. Kirby*, P. Byrne, M.J. Stalker, I.R. Smith and M.A. Hayes, University of Guelph, Guelph, Ontario 302

B14 **The Use of Benthic Invertebrates in Mapping Toxic Areas of Sediment and Determining the Efficacy of Sediment Cleanup Operations;** M. Dickman*, F. Fiore and I. Brindle, Brock University, St. Catharines, Ontario 317

B15 **Monitoring of Organic Contaminants in Aquatic Food-Chains;** G.D. Haffner*, F.A.P.C. Gobas, R. Lazar and D. Laviolet, University of Windsor, Windsor, Ontario 327

B16 **PCB Dynamics of Pottersburg Creek, London, Ontario;** D.T. Zaranko*, K.R. Solomon and N.K. Kaushik, University of Guelph, Guelph, Ontario 328

VOLUME I

SESSION B: WATER QUALITY RESEARCH

Poster Presentations **Page**

BP1 **Development of an Improved System for the Application of Powdered Activated Carbon in Potable Water Treatment;** H.E. Donison and A. Benedek, ZENON Environmental Inc., Burlington, Ontario 340

BP2 **Geochemical Associations of Cd, Cu, Pb and Zn with Suspended Particulates in the Don River;** L.A. Warren and A.P. Zimmerman, University of Toronto, Toronto, Ontario 343

BP3 **The Effects of Agricultural Drainage on Sediment and Water Quality Loadings;** J.D. Paine, W.E. Watt and S.A. Peters, Queen's University, Kingston, Ontario 344

BP4 **Chronic Effects of Thiocyanate on Freshwater Fish: Development of a Water Criterion;** R.P. Lanno and D.G. Dixon, University of Waterloo, Waterloo, Ontario 349

BP5 **Zooplankton Communities and Water Chemistry of Sudbury Area Lakes: Changes Related to pH Recovery;** A. Locke and W.G. Sprules, University of Toronto, Mississauga, Ontario 358

BP6 **The Relative Effect of Individual Environmental Factors on Indicator Bacterial Survival;** E. Harris, Lake Simcoe Region Conservation Authority, Newmarket, Ontario 359

Volume I **Page**

BP7 **The Effect of Farm Liquid Waste Application on Receiving Water Quality;** D.M. Dean and M.E. Foran, Ausable Bayfield Conservation Authority, Exeter, Ontario 365

BP8 **Statistical Assessment of Multivariate Ordination Techniques for Zoobenthic Communities and Water Chemistry for Lakes from Central Ontario;** D.A. Jackson and H.H. Harvey, University of Toronto, Toronto, Ontario 370

BP9 **Geochemical Alteration of Road De-Icing Chemicals by Sub-Surface Rock-Soil-Water Interactions;** K.W.F. Howard and J. Haynes, University of Toronto, Scarborough, Ontario 371

BP10 **Standardized Rearing Materials and Procedures for Hexagenia, a Benthic Bioassay Organism: Comparison of Sediment Types;** E.C. Hanes, J.J.H. Ciborowski and L.D. Corkum, University of Windsor, Windsor, Ontario 374

BP11 **Tillage and Event Based Soil and Water Loss: Scale Linkages;** R.G. Kachanoski, W.T. Dickinson and R. Rudra, University of Guelph, Guelph, Ontario and University of Waterloo, Waterloo, Ontario 383

BP12 **Validation of Spottail Shiner Daily Otolith Rings;** P.M. Powles, B.A. Powles and R.A. Curry, Trent University, Peterborough, Ontario 386

BP13 **An Investigation of the Potential of Zygnematacean Zygospores, Peridinium, and Pediastrum as Paleo-Indicators of Recent Lake Acidification;** P. Zippi, Y-K Yung, J.A. McAndrews, G. Norris and P. Welbourn, University of Toronto, Toronto, Ontario 393

VOLUME II

INDEX

Keynote Presenters **Page**

Sustainable Development: The Technological Challenge; Noel J. Brown, Director, United Nations Environment Programme 397

Responses to Global Climate Change: The Coming Environmental and Economic Revolutions; Jim Bruce, Chair, Canadian Climate Program Board 398

Feature Presenters

Air Quality Research

A1 **What's the Latest on Acidic Deposition in North America?;** D. Sisterson, Argonne National Laboratory, Argonne, Illinois, USA 401

A10 **Measurement of Semi-Volatile Organic Compounds in Ambient Air;** G. Hunt, ENSR, Acton, Massachusetts, USA 403

Water Quality Research

B1 **Influence of the Zebra Mussel *(Dreissena polymorpha)* on Water Quality of Lake Erie;** J. Leach, Ontario Ministry of Natural Resources, Wheatley, Ontario 404

B10 **Cross-Disciplinary Analyses of Environmental Health Studies Suggest the Need for New Approaches to Risk Assessment;** T. Colborn, US Conservation Foundation, Washington D.C., USA 406

Volume II **Page**

Liquid & Solid Waste Research

C1 **Environmental Concerns - Keeping our Perspective;** J.P. Nunan, Trow, Dames & Moore, Mississauga, Ontario 408

C10 **Oxidation to Remove Trichloroethylene from Soil;** G. Farquhar, University of Waterloo, Waterloo, Ontario 412

Analytical Methods Research

D1 **Ion Mobility Spectrometry in Atmospheric Environmental Monitoring in the U.S. Space Program;** G.A. Eiceman, New Mexico State University, Las Cruces, New Mexico 413

Environmental Socio-Economics

E1 **Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market;** B. Hull, The Conference Board of Canada, Ottawa, Ontario 415

Multimedia Contaminants & Biotechnology

F1 **Utilization of Environmental Research to Control Lead Contamination;** B.G. Wixson, Clemson University, Clemson, South Carolina, USA 416

Panel Presentations

Global Warming: What is at Stake?

P1 **The International Scene;** J.P. Bruce, Chair, Canadian Climate Program Board 422

P2 **Global Warming: A Canadian Perspective and Action Strategy;** D.K. Dawson, Director General, Canadian Climate Centre 423

Volume II

		Page
P3	**Global Warming: What is at Stake? Socio-Economics;** E. Haites, Barakat & Chamberlin Inc.	424
P4	**Warming to a Crisis: The Media and Climate Change;** M. Keating, Environmental Writer	428
P5	J.D. McFarland, Imperial Oil Limited	432
P6	**Global Warming: What's Known and What's Not?;** B. Yang, Ontario Cabinet Office	433

VOLUME II

SESSION C: LIQUID & SOLID WASTE RESEARCH

Verbal Presentations Page

C2 **Manual for Establishing Vegetation on Erosion-Prone Landfill Slopes in Ontario;** N. DeFraeye* and T.W. Hilditch, Gartner Lee Limited, Markham, Ontario 434

C3 **Quantification of Infiltration Through Landfill Covers;** K.J. McKague*, Ecologistics Limited, Waterloo, Ontario and J.H. Cuthill, University of Guelph, Guelph, Ontario 442

C4 **Accurate Control Testing for Clay Liner Permeability;** R.J. Mitchell, Queen's University, Kingston, Ontario 456

C5 **Field Demonstration of Membrane Technology for Treatment of Landfill Leachate;** C.M. Smith* and T.A. Krug, Zenon Environmental Inc., Burlington, Ontario 464

C6 **Slow Rate Infiltration Land Treatment and Recirculation of MSW Landfill Leachate in Ontario;** R.A. McBride*, A.M. Gordon, P.H. Groenevelt, T.J. Gillespie and L.J. Evans, University of Guelph, Guelph, Ontario 475

C7 **Determination of Hydro-geological and Contamination Transport Properties of Fractured Weathered Leda Clay in Eastern Ontario;** A.Y. D'Astous*, Envir-Eau Inc., Hull, Quebec and N.G. Castonguay, Fondex Ltd., Nepean, Ontario 485

Volume II **Page**

C8 **The Characterization of Two Discrete Horizontal Fractures in Shale;** P.A. Lapcevic* and K.S. Novakowski, National Water Research Institute, Burlington, Ontario and J.A. Cherry, University of Waterloo, Waterloo, Ontario **486**

C9 **The Origin and Distribution of Methane in the Alliston Sand Aquifer Complex;** R. Aravena*, L. Wassenaar, J. Barker and R.W. Gillham, University of Waterloo, Waterloo, Ontario **496**

C11 **The Recycling of Steelmaking Dusts Using the LB Furnace;** Q.S. He, C. Bryk and W.K. Lu*, McMaster University, Hamilton, Ontario **505**

C12 ***In Situ* Biodegradation of Chlorinated Solvents;** D.W. Major* and E.W. Hodgins, Beak Consultants Limited, Guelph, Ontario **518**

C13 **Glassification and Leachability of Hazardous Wastes and Hazardous Waste Residues;** K.B. Harvey, AECL Research, Whiteshell Laboratories, Pinawa, Manitoba **519**

C14 **Non-Linear Sorption of Phenol on Natural Clay and its Influence on Diffusive Migration;** J.P. Mucklow* and R.M. Quigley, The University of Western Ontario, London, Ontario **520**

C15 **Estimating Landfill Leachate and Contaminant Production;** L. Jarvis* and G. Farquhar, University of Waterloo, Waterloo, Ontario **530**

C16 **Test of a Chemical Mechanical Process for the Decontamination of Non-Anatomical Biomedical Waste;** P.L. Seyfried*, T. Bleier, S. Qaiyumi, B.-L. Xu, N. Anderson, C.C. Tse, and N. Azami, University of Toronto, Toronto, Ontario **540**

VOLUME II

SESSION C: LIQUID & SOLID WASTE RESEARCH

Poster Presentations Page

CP1 **Purification and Detoxification of Textile Dyebath Effluent by Electrochemical Treatment;** A.E. Wilcock, University of Guelph, Guelph, Ontario 548

CP2 **Stabilization of a Waste in a Landfill Environment;** M. Modi and D.W. Kirk, University of Toronto, Toronto, Ontario 553

VOLUME II

SESSION D: ANALYTICAL METHODS RESEARCH

Verbal Presentations **Page**

D2 **Coupling an External Source to a Fourier Transform Ion Cyclotron Resonance Spectrometer to Improve its Use for Analytical Purposes;** T.B. McMahon* and C.E.C.A. Hop, University of Waterloo, Waterloo, Ontario 557

D3 **The Analysis of N-Nitrosodimethylamine in Environmental Samples by GC-MS;** J.-P. Palmentier*, V. Taguchi, E.J. Reiner, S.W.D. Jenkins, D.T. Wang, D. Robinson, R.J. Kleins and K.-P. Ngo, Environment Ontario, Rexdale, Ontario 558

D4 **Real Time Measurements of Dimethylnitrosamine in Ambient Air by Mobile Tandem Mass Spectrometry;** N.S. Karellas*, G.B. DeBrou and A.C. Ng, Air Resources Branch, Environment Ontario, Toronto, Ontario 561

D5 **The Analysis of Smithville Drinking Water for PCBs;** D. Sutherland*, J. Waugh, L. Paul, A. Rayner and G. Reuel, Canviro Ltd., Kitchener, Ontario 569

D6 **Evaluation of Environmental Sources of Polychlorinated Biphenyls Using Chemometric Methods;** S. Davies*, Laboratory Services Branch, Environment Ontario, Toronto, Ontario and F. Onuska, Environment Canada, Burlington, Ontario 574

Volume II Page

D7 **Isolation and Derivatization of Chloro-Aromatic Organic Acids on Solid Support;** J. Rosenfeld* and Y. Maharir, McMaster University, Hamilton, Ontario 584

D8 **Bias Due to Sampling Ground-Water and Surface Water for Trace Organic Contaminants;** J.T. Hoff*, C. Arthur, D. Baerg, J.F. Barker and R.W. Gilham, University of Waterloo, Waterloo, Ontario 592

D9 **Polynuclear Aromatic Hydrocarbons Identification Using GC/FT-IR and Pairs;** J. Semmler*, P. Yang and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 601

D10 **The Struggle Towards Virtual Elimination of Toxic Chemicals from the Environment;** D. MacKay, University of Toronto, Toronto, Ontario 615

D11 **Graphical Techniques for the Presentation of Inter-laboratory Study Data-A Diagnostic Aid;** S. Cussion* and D.E. King, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 618

D12 **Design, Constraints and Implementation of Rules Within ACexpert;** M.J. Stillman*, S. Lahiri and Q. Zhu, The University of Western Ontario, London, Ontario 628

D13 **An Apparatus for Rapid Microwave Sample Decomposition;** V. Karanassios*, F.H. Li and E.D. Salin, McGill University, Montreal, Quebec 640

Volume II **Page**

D14 **An Electrothermal Vaporization System for the Direct Analysis of Solids by ICP-AES;** E.D. Salin*, V. Karanassios and J. Ren, McGill University, Montreal, Quebec 648

D15 **Flow Injection Preconcentration/ Direct Sample Insertion for Trace Element Analysis by ICP-AES and ICP-MS;** P. Moss* and E.D. Salin, McGill University, Montreal, Quebec 655

D16 **Prereduction of Arsenic (V) to Arsenic (III), Enhancement of the Signal, and Reduction of Interferences by L-Cysteine in the Determination of Arsenic by Hydride Generation;** I.D. Brindle*, Brock University, St. Catharines, Ontario and H. Chen, Hangzhou University, Peoples Republic of China and X-C. Le, University of British Columbia, Vancouver, British Columbia 663

VOLUME II

SESSION D: ANALYTICAL METHODS RESEARCH

Poster Presentations **Page**

DP1 **Expert Systems in Analytical Chemistry. Design of a User Interface and Implementation of Rules for ACdiagnosis within ACexpert;** S. Lahiri, Q. Zhu and M.J. Stillman, University of Western Ontario, London, Ontario **672**

DP2 **Development of a Turn-Key System for Hazardous Wastes Analysis;** P. Yang, M. Yang, J. Semmler and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario **676**

DP3 **Study of the Effect of Solvent and Stationary Phase on the Chromatographic Behavior of PAHs;** I.D. Brindle and X. Li, Brock University, St. Catharines, Ontario **688**

DP4 **Monitoring Ambient Air VOCs Using Cryogenic and Adsorbent Trap: A Critical Evaluation;** P. Yang, L. Au, P. Ford, B. Foster and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario **694**

DP5 **Adaptation of Water Preconcentration Techniques Developed for PCDD Analysis to Other Target Organic Pollutants;** C. Shewchuk, L.J. Brownlee and B.R. Hollebone, Carleton University, Ottawa, Ontario **701**

Volume II **Page**

DP6 **Complete Ambient Air VOCs and VOST POHCs Analyses Using One Single TD/GC/MS System;** L. Au, S. Kullar, P. Yang, P. Ford, B. Foster and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 707

DP7 **An Automated Gel Permeation Chromatographic Method for Cleanup of Sewage Sludge Extracts for GC/MS Analysis of Priority Organic Pollutants;** R. Lega, M. Meconnen, A. Salewski, G. Crawford, O. Meresz and I. Ahmad, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 716

DP8 **Simultaneous Derivatization – Extractions Technique for the Analysis of Acidic Organic Contaminants from Water – Feasibility Study with Diazomethane for the Analysis of 4-Amino – 3,5,6-Trichloro Picolinic Acid (Picloram);** R. Lega, O. Meresz and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 722

DP9 **Brominated and Mixed Bromo/Chloro Dibenzo-p-Dioxins and Dibenzofurans: Toxicological Properties, Analytical Methods and Occurrence;** B.G. Chittim and D.S. Waddell, Environmental Consultants Incorporated, Guelph, Ontario 727

Volume II **Page**

DP10 **Determination of Organolead Compounds in Industrial Effluents;** M.J. Powell, I. Ahmad and L. Glassford, Environment Ontario, Rexdale, Ontario 730

DP11 **Techniques for Identification of Specific Sources of Airborne Particulates;** T. Lee, R. Martin and M. Giuliacci, University of Western Ontario, J. Hipfner and R. Moody, Laboratory Services Branch, Environment Ontario, Toronto, Ontario 735

VOLUME II

SESSION E: ENVIRONMENTAL SOCIO-ECONOMICS

Verbal Presentations

Page

E2 **Tradable Permits for the Control of Sulphur Oxides in Canada;** C.D. Mallory, Environment Canada, Montreal, Quebec 740

E3 **Estimating Public Benefits of Implementing the Proposed Revisions to Regulation 308;** E.F. Haites*, Barakat & Chamberlin, Toronto, Ontario and P.A. Blyth, Environment Ontario, Toronto, Ontario 753

E4 **Recycling, Reducing and Reusing: A Theoretical Framework;** A.A. Kubursi* and D.W. Butterfield, Econometric Research Limited, Oakville, Ontario 765

E5 **The Economic Implications of the Zebra Mussel *(dreissena polymorpha pallas)* Invasion of the Great Lakes;** J.A. Donnan* and C.E. MacKay, Environment Ontario, Toronto, Ontario 775

E6 **Economics and Technical Change: The Water Resource Conundrum;** D. Tate*, Environment Canada, Ottawa, Ontario and R. Rivers, Environment Canada, Burlington, Ontario 790

E7 **Modelling Municipal Water Systems for Demand Management;** E.E. Creese* and J.E. Robinson, Environment and Resource Studies, University of Waterloo, Waterloo, Ontario 800

Volume II **Page**

E8 **Economic Analyses of Ontario's Water Pollution Control Initiative for Direct Industrial Dischargers;** O.E. Salamon*, J.A. Donnan, P.A. Blyth and L.M. Coplan, Environment Ontario, Toronto, Ontario 806

E9 **The Impacts and Effects of the Hagersville Tire Fire: Preliminary Analysis and Findings;** J. Eyles*, et al, McMaster University, Hamilton, Ontario (D. Sider, N. White, D. Willms, S.M. Taylor, D. Streiner, S. Walter, S. Elliott, J. Frank and M. Haight) 818

VOLUME II

SESSION F: MULTIMEDIA CONTAMINANTS & BIOTECHNOLOGY

Verbal Presentations

Page

F2 **Regulating a Multi-media Contaminant: US EPA's Lead Strategy;** R. Levin, Environmental Protection Agency, Washington, D.C., USA 830

F3 **Application of a Multimedia Risk Assessment Approach to Ontario Soil Contamination Cases;** S. Fleming*, Hazardous Contaminants Coordination Branch, Environment Ontario, Toronto, Ontario 839

F4 **A Fugacity Model of Chemical Fate in an Uncertain Multi-media Environment;** D. Mackay*, S. Paterson and W. Stiver, University of Toronto, Toronto, Ontario 848

F5 **Pollutant Interactions in Mutagenicity Testing;** D.M. Logan* and A.S. Raj, York University, North York, Ontario 864

F6 **Genotoxic Compounds Associated with Respirable Urban Air Particulate. Chemical Fractionation and Bioassay of Complex Mixtures;** D.W. Bryant*, B.E. McCarry and D.R. McCalla, McMaster University, Hamilton, Ontario 874

F7 **Ministry Research Needs in Biotechnology;** J.S. Bailey, Hazardous Contaminants Coordination Branch, Environment Ontario, Toronto, Ontario 885

VOLUME I

KEYNOTE PRESENTATIONS

Keynote Paper I

Sustainable Development: The Technological Challenge

Noel J. Brown, Director, United Nations Environment Programme, North America

PAPER NOT AVAILABLE AT TIME OF PRINT

"RESPONSES TO GLOBAL CHANGE:
the Coming Environmental and Economic Revolutions"

Keynote address: J. P. Bruce

Environmental Research: Technology Transfer Conference
Toronto, 19-20 November 1990

Extended Abstract:

The Intergovernmental Panel on Climate Change has provided in 1990, the most definitive scientific assessment to date of the changes in greenhouse gas concentrations in the atmosphere and the probable effects on the world's climate. This consensus report of more than 300 scientists from many countries, places the major conclusions in 4 main categories of descending degrees of scientific certainty. The Panel is certain that in the atmosphere and that human activities are substantially increasing greenhouse gas concentrations in the atmosphere and that the natural radiation exchanges known as the "greenhouse effect", are real. They "calculate with confidence" that CO2 has caused and will continue to produce more than half of the human-enhanced greenhouse effect, and that the long-lived gases, (CO2, nitrous oxides and the CFC's) would require immediate emission reductions of more than 60% to stabilize atmospheric concentrations at present levels. They predict, based on current model results, that if nothing is done, i.e. a "business-as-usual" scenario prevails, global mean temperatures will rise 0.3 degrees C per decade (with a range of 0.2 to 0.5 degrees C) and sea level will rise 6 cm per decade (range 3-10cm) over the next century. These are rates greater than ever experienced since man first tilled the soil, some 10,000 years ago. Northern latitudes and large land areas, like central and northern North America, are predicted to warm more rapidly than the global mean. The impacts of such changes on coastal communities, small islands, water resources, agriculture, forestry, the spread of tropical diseases, would be increasingly profound over the next 100 years. At their lowest level of certainty, they advise that their judgement is that the mean global temperature has already risen 0.3 degrees to 0.6 degrees C over the past 100 years, "broadly consistent with predictions of climate models".

Responses to this prospect have, on the one hand, been widespread alarm, especially on the part of low lying island countries and ones with extensive low coastlines, and countries with only marginal agriculture and water resources. Spokesmen for other countries, such as USSR, see a somewhat warmer climate as mostly advantageous. A number of western European countries, and scattered sub-national jurisdictions elsewhere have already announced plans to cut CO2 emissions, and some, including Canada, have committed themselves to a stabilization of emissions.

However, most agree that concentrated, coordinated international actions are needed to really reduce the rate of accumulation of greenhouse gases and attention is now focussed on negotiation of a global convention on climate change, hopefully by the item of the UN Conference on Environment and Development in Brazil, June 1992. The urgency is great, since as the IPCC points out, if nations can cut CO2 emissions by 2% per annum beginning in 1990, concentrations will be stabilized at 390 parts per million by 2020 or so, but if cuts are delayed 20 years, stabilization will not occur until 2070, and then at a much higher 460 ppm.

There are four major contentious issues which will have to be resolved in negotiations of a Convention on Climate Change. These are:

1) a plan to cut greenhouse gas emissions, especially CO2;
2) a plan to move from net global deforestation to afforestation;
3) transfer of funds or other economic incentives to permit developing countries to make the necessary investments and adjustments, and
4) transfer to developing countries on a preferred basis, of low emission technologies.

All of these issues have potentially enormous economic as well as environmental implications.

The first will require, above all, a major change in energy policies of the nations, especially the highest per capita energy users, Canada and USA. The key requirements are aggressive conservation strategies driven by end-use oriented services rather than the supply side, and switching to lower CO2 emitting fuels, away from oil and coal. Examples of what is achievable at low net cost in North America and India will be outlined.

In the business world, our major industrial competitors, in Europe and Japan, are already much more energy efficient than North America, and are adopting even greater efficiency measures. There is every reason to fear for the future competitiveness of Canada and USA if energy efficiency is not pursued vigorously in the next few decades.

The third of these issues is one stressed by developing countries in all of the pre-negotiation meetings. Without major initial financial investments, they will be unable to institute the energy efficiency, fuel switching and reforestation measures needed to prevent them from augmenting greenhouse gas emissions at a rapid rate to meet the increasing needs and expectations of their people. Such investments are clearly impossible in a world in which the net financial flow is away from the developing world with low commodity prices and huge debts, to the industrialized countries. This flow must be reversed, or at a minimum a major fund, greatly exceeding the $270 million committed to a CFC replacement fund, will be required to permit the developing countries to be full partners in a world-wide effort to protect the global atmosphere.

The recent success of the world community, in agreeing to a strengthened plan for CFC emission controls to protect the ozone layer under the Montreal protocol lends some optimism to the prospect of a more comprehensive climate change convention. It also buys a little time through CFC reductions to put in place the more difficult CO2, methane and nitrous oxide controls.

However, the major issues on the table can only be resolved if the industrialized countries accept their responsibility to greatly reduce their own greenhouse gas emissions, increase afforestation, and assist developing countries to do the same. Revolutions in our thinking about, and use of, energy, and in our relationships with developing countries are urgently needed if we are to protect the atmosphere of our small planet and the climate it produces.

VOLUME I

FEATURE PRESENTATIONS

A1

WHAT'S THE LATEST ON ACID DEPOSITION IN NORTH AMERICA?

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This presentation summarizes the results of the National Acid Precipitation Assessment Program State of Science/Technology Report Deposition Monitoring: Methods and Results (Sisterson et al. 1990). The larger document discusses methods to monitor wet, dry, and droplet deposition in the United States and Canada and provides temporal and spatial analyses for the period 1979-1987. A significant portion of the document addresses the representativeness and completeness of large-scale network deposition data at regional and local scales.

The most complete deposition monitoring results are for wet deposition. Information on dry deposition is insufficient to allow spatial and temporal analyses on a regional scale of the major acidic deposition species and their precursors. Information on droplet deposition (i.e., deposition by interception of cloud water and fog droplets, sometimes called "occult" deposition) is even more recent than that on dry deposition, and little information exists for spatial and temporal analyses except at a few sites.

The areas of maximum wet deposition of individual inorganic chemical species in precipitation are located in the northeastern United States and southeastern Canada, and those locations have not changed significantly in the past decade. The weight of scientific evidence suggests that all analytes except pH or acidity exhibited a decreasing (not statistically significant) trend in deposition and concentration in 1979-1987 for the eastern half of the United States and Canada. Median annual precipitation-weighted concentrations are larger in North America than in remote regions of the world by factors of 9 for SO_4^{2-}, 14 for NO_3^-, 7 for NH_4^+, and 4 for H^+. The average pH of precipitation in remote regions of the world is closer to 5.0 than to 5.6. Excluding precipitation monitoring sites from urban areas and the influence of major local sources causes the integrated wet deposition chemistry estimates to be low.

The finding that sulfur and nitrogen species in precipitation have decreased but pH has not changed is perhaps the single largest surprise of the State of Science Report. A large decrease in calcium and other base cations offsets decreases in acid species in precipitation. The reason for the decrease in calcium is not clear. In part, it can be attributed to changes in agricultural practices, paving of rural gravel highways, and perhaps emission controls; the same emission controls that remove sulfur and nitrogen species from smokestacks may also remove base cations such as calcium that reduce precipitation acidity.

Preliminary results indicate that dry deposition for sulfur is between 0.3 and 0.5 of the wet plus dry deposition at regionally representative sites and is between 0.3 and 0.7 for nitrogen. Most of the dry-deposited sulfur is due to SO_2, with values of 50-90%. Most of the dry-deposited nitrogen is due to HNO_3, with values of 76-88%. The ratio of dry plus wet deposition of sulfur species to that of nitrogen species varies between 4.25 and 0.77.

Concentrations of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ are 5-20 times larger in cloud water at high-elevation sites than in precipitation. Droplet deposition of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ is up to three times wet plus dry deposition in the warm season for high-elevation sites that are frequently in cloud. High-elevation sites above 600 m experienced in-cloud conditions 30-40% of the time during the growing season (April-October). The liquid water content averaged about 0.20 g m^{-3} at most sites.

By using these wet, dry, and droplet deposition data together with anthropogenic emissions and an estimated urban perturbation factor for wet and dry deposition, S and NO_x-N mass budgets were determined (Venkatram et al., 1990). For all of the United States and Canada combined, 39% of anthropogenic SO_x-S emissions were accounted for by wet deposition, 23% by dry deposition, and 4% by droplet deposition, and 34% of the emissions were exported from North America. For NO_x-N, 40% of anthropogenic emissions were accounted for by wet deposition, 26% by dry deposition, and 3% by droplet deposition, and 34% of the emissions were exported from North America. The urban perturbation accounts for 15% of the wet plus dry deposition for the United States and Canada combined.

It is interesting to note that both sulfur and nitrogen species in precipitation in Canada in this study exceed Canadian emissions, probably due to the overall net transport of emissions from the United States into Canada.

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Sisterson, D.L., V.C. Bowersox, A.R. Olsen, T.P. Meyers, and R.J. Vong. 1990. Deposition Monitoring: Methods and Results. SOS/T Report 6, National Acid Precipitation Assessment Program, Washington, D.C.

Venkatram, A., D. McNaughton, and P.K. Karamchandani. 1990. Relationships between Atmospheric Emissions, Acidic Deposition, and Air Concentrations. SOS/T Report 8, National Acid Precipitation Assessment Program, Washington, D.C.

A10 Measurement of Semi-Volatile Organic Compounds in Ambient Air; G. Hunt, ENSR, Acton, Massachusetts, USA

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B1

ABSTRACT

Leach, J.H., Ontario Ministry of Natural Resources, Lake Erie Fisheries Station, R. R. #2, Wheatley, Ontario, N0P 2P0. Influence of the zebra mussel, Dreissena polymorpha on water quality of Lake Erie.

The European zebra mussel, Dreissena polymorpha (Pallas), is now well established in the Great Lakes system. Initial colonization may have occurred in 1986, likely from larvae discharged in ballast water, but mussels were not observed in Lake St. Clair and Lake Erie until June 1988. Large populations of the mussel are now established in these lakes. It has spread to all of the Great Lakes and is found from Cornwall, Ontario, in the east to Duluth, Minnesota, in the west. Dispersion has been aided by a motile larval stage and the ability of adults to attach to boat hulls with byssus threads.

The zebra mussel is a serious biofouling pest in Europe and is rapidly becoming one in North America. One of its most harmful impacts is the colonization of intake cribs and pipes serving water treatment plants, power generating stations and industries. Costs associated with prevention of infestations and removal of encrustations are projected at many millions of dollars.

Ecological impacts are also possible but are more difficult to predict and quantify. There is concern that some species of native mussels, and in particular the large unionids, may be in jeopardy because their shells are being colonized to the point where the mussels can no longer function normally. Although impacts on fisheries have not yet been measured, managers are concerned that the invader could affect fish production in two ways. The fouling of spawning reefs could affect reproduction of shoal spawners if the habitat is altered sufficiently to reduce egg deposition and survival. Preliminary results from observations on walleye in the western basin of Lake Erie indicated that reproduction and survival in 1990 were satisfactory. Secondly, the shifting of organic matter from pelagic to benthic areas through filtering by zebra mussels could disrupt the food web that links primary production to larval fish. Research to quantify this process and to determine its impact on the food web is currently underway in Lake Erie.

The zebra mussel has already affected water quality in Lake Erie and Lake St. Clair. The most visual impact is an increase in water clarity. Between 1988 and 1989 (May to November), mean Secchi disc transparencies increased 85 percent and 52 percent in the western and central basins of Lake Erie respectively. Preliminary data to September 1990 indicate that mean transparencies in 1990 were still greater than those in 1988 but less than those recorded in 1989. Resuspension of bottom sediments due to above normal winds during spring and early summer of 1990 probably masked the effects of the zebra mussels on water clarity. For example, transparencies in the western basin in August and September, 1990, were above those measured in the same period in 1989. Turbidity in Rondeau Bay has declined to the point where water clarity is probably sufficient to permit rooted aquatic plants to reestablish.

Mean concentrations of chlorophyll *a* declined 43 percent and 27 percent in the western and central basins of Lake Erie respectively between 1988 and 1989 (May to November periods). Preliminary results indicate a further decline in 1990, especially in the western basin. *Dreissena* is obviously competing successfully with filter feeders for phytoplankton. The production of faeces and psuedofaeces by *Dreissena* should favour other benthic organisms and early observations indicate an increase in gammarids in western basin reef areas. There is concern that a build-up of organic matter in the interstitial areas around the mussels could reduce dissolved oxygen concentrations through decomposition to the point where survival of fish eggs was adversely affected. However, a joint study with the Department of Fisheries and Oceans in April, 1990, indicated that dissolved oxygen was at or near saturation levels on walleye spawning reefs in the western basin of Lake Erie. Further studies are required to determine what happens to oxygen concentrations as organic matter and layers of mussels accumulate.

There are early indications that water taste and odour may be affected at water treatment plants (WTP) by *Dreissena*. Taste and odour problems occurred at the Windsor WTP in the summer of 1990 and were attributed to *Dreissena* either directly from the bodies of veligers and adults or indirectly from increased populations of aquatic plants because of improved water clarity. Additional research is required to delineate causes of taste and odour problems and also to determine to what extent *Dreissena* is improving water quality by concentrating contaminants.

B10

CROSS-DISCIPLINARY ANALYSES OF ENVIRONMENTAL HEALTH STUDIES SUGGEST THE NEED FOR NEW APPROACHES TO RISK ASSESSMENT

by

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A comprehensive examination of the literature on wildlife and human health in the Great Lakes basin provides incentive for new approaches to assess hazard from exposure to bioaccumulative, toxic substances. A review of the mechanistic actions of the contaminants commonly found in wildlife and human tissue further supports the need for change. Current public health strategies to measure population effects are too blunt to detect the subtle health decrements that may occur as a result of exposure to these chemicals. Breakthroughs in understanding the effects of a number of these persistent, pervasive organic chemicals are being made in the Great Lakes region by integrating research in wildlife, human, veterinary, and animal toxicology, ecology, epidemiology, and cellular and tissue biology. Following years of monitoring contaminants in the ecosystem, researchers in these disciplines are beginning to interpret what the concentrations mean in terms of wildlife health effects. This information provides new tools for public health authorities to assess the status of human health.

Sixteen top predator species in the Great Lakes basin have experienced severe reproductive problems accompanied by population declines since the 1950s. The health of many bird species showed marked improvements in the 1970s as the result of reductions in DDT and its metabolites producing thicker egg shells and improved reproductivity. Today, health problems that are just as serious but far more subtle than eggshell thinning are still reported in top predator species. Few overt symptoms are reported in adult animals -- instead, they are observed in offspring of exposed animals.

Health problems observed in wildlife offspring have been associated with elevated exposure to a number of contaminants. Researchers infer this exposure is the result of parental transfer through the egg, placenta, breast milk, and/or feeding of contaminated prey to offspring. Anomalies reported in wildlife offspring include: metabolic problems that cause low birth weight, loss of weight gain, and in some instances death from wasting; edema; birth defects; embryo, chick, fetus, neonate, and young adult mortality; behavioral changes; target organ damage; immune suppression; and abnormal sexual development.

An examination of the literature on the chemicals most often found in both Great Lakes wildlife and human tissues was undertaken. With one exception, (benzo a pyrene) these contaminants are not acute toxicants and genotoxicants, nor have they been determined unequivocally to be human carcinogens. They are developmental toxicants. Research at the cellular and tissue level shows that the mechanisms of action of the critical Great Lakes pollutants are often similar and general in nature. Most of the critical chemicals found in elevated concentrations in Great Lakes biota are capable of affecting normal metabolism and development in at least one or all of the following ways. First, they block cell to cell communication. Second, they induce enzymes in a number of tissues that enhance the excretion of hormones naturally produced by the endocrine system. And third, because of their chemical structure they have an estrogenic influence as well. All three mechanisms under proper timing and dose can lead to abnormal development. The cumulative effect of mixtures of these chemicals at the cell, tissue, and organ level is just beginning to be understood.

It is important to note that in laboratory animals a number of developmental health decrements have been associated with specific PCB, dioxin, and furan congeners and a number of pesticides including DDT and its metabolites, dieldrin, lindane, hexachlorobenzene, and others. These adverse health effects include wasting, edema, birth defects, immune suppression, target organ damage, effeminization of male animals, behavioral changes, and premature death, all in a dose-related manner; the same health decrements reported in Great Lakes wildlife.

Most importantly, except for a few fish species and the Beluga whale, cancer has not been reported in Great Lakes animals. Unfortunately, most risk assessments are based on cancer, not developmental effects, with the exception of mercury and lead.

A global search of the literature on residues of these contaminants in human tissues reveals they are found in all reproductive tissue, including breast milk. As a result, exposure during the embryo, fetal, and perinatal periods can be elevated on a weight to weight basis, coinciding with a period of rapid development that sets the course of development through maturity. Recent laboratory studies using a number of these chemicals revealed that obvious health effects may not be fully manifested until adulthood in exposed animals. Using wildlife and animal studies as models to assess human health, new technologies are needed to measure human exposure as well as new approaches to measure the possible cognitive, behavioral, and social effects of developmental toxicants.

C1

ENVIRONMENTAL CONCERNS - KEEPING OUR PERSPECTIVE

John P. Nunan, P.Eng., President
Trow, Dames & Moore

INTRODUCTION

This talk is intentionally provocative. The purpose of the presentation is to put before you a number of current, relatively high-profile, environmental concerns, and to discuss these in brief so as to stimulate thinking as to the type of research that might be undertaken to enhance knowledge of these issues, and putting them in truer perspective as they may affect public health and safety, and the quality of our physical environment.

Four concerns (issues) have been selected for discussion, not necessarily because of their importance, but rather due to the fact that these issues have been around for some time with little growth in our understanding of their true significance and seriousness. They are also issues that are causing much concern to various segments of the community and expenditures of large amounts of money to mitigate, possibly with less than adequate understanding as to why or if such mitigation is effective, or really required.

As Professor P.H. Jones has said, "society is engulfed in fear". This fear is not based on scientific findings, which have demonstrated that harm can result. It is based more on our ability to detect certain substances in our environment which we have discovered can adversely affect humans if ingested in large quantities. It is wrong to equate, in the minds of the public, the mere detection of a substance with ghastly public health threats. Such concerns have tremendously complicated life and in several instances have brought some forms of desirable development to a grinding halt. Some specific issues causing these concerns will now be discussed.

1) Methane Gas

Methane is a naturally occurring light hydro-carbon gas that results from the biodegradation of carbonatious material in the absence of oxygen. Methane is very widespread in nature and comprises approximately 95 percent of natural gas. Methane is produced in significant quantities during anaerobic decomposition of solid wastes in garbage dumps. It is also produced in earth fills where relatively small quantities of biodegradable material such as grass, brush and swamp debris has been incorporated in the fill. Methane can migrate from its location of generation to accumulate in buildings and other works where ignition of the gas has resulted in destruction of buildings and loss of life.

Today, the measure of a methane hazard or risk is usually determined by the insitu concentration of the gas. Is this appropriate? Is there a better way to evaluate the hazard? Is it really necessary to restrict development as much as we now do because of the presence of high insitu concentrations of methane? Are there, or can there be developed reliable methods of measuring methane flux directly, which, when compared to conservative estimates of building ventilation, will show when a buildup of methane is so improbable that development of a particular site should not be constrained?

The issue of methane recovery from large, or even small garbage dumps, seems to offer a potentially attractive opportunity for energy recovery. This is already being achieved at some very large landfills, where the cost of energy is high and a suitable market for that energy is available. Some of the questions that need to be answered through research include: What are the conditions that enhance the rate of methane production? Is it better to keep landfill dry so as to restrict the rate of methane production, which also delays stabilization of the landfill, or is it preferable to develop sanitary landfills so as to enhance methane production? How would the recovery and use of methane from a landfill, where methane production was intentionally enhanced, compare economically with other forms of waste recycling for energy, conservation and recovery, such as the burning of refuse-derived fuel from waste? What do we know about the character of the solid waste that goes into our Canadian landfills? Are we perhaps missing opportunities or even aggravating conditions by some current practices such as removal of materials from waste streams that would produce methane, when the cost of reusing these materials in other ways is less attractive?

2) Nitrates In Groundwater

Nitrate which is an essential compound for plant growth and which is naturally produced in the environment by bacterial activity and to a much smaller degree, by electrical storms in the atmosphere, has become a major concern relative to the potable use of groundwater. The use of nitrate in fertilizers to increase food crop yields in rural areas and the heavy use of nitrogen fertilizers to grow green lawns in urban areas is increasingly suspected as being the cause of nitrate buildup in groundwater, which in many areas has risen to fifty percent, or more, of the accepted 10 ppm for drinking water. This change has caused concern that the trend will continue, which in turn has resulted in rejection of some well supplies intended for municipal use, even though all other quality and quantity factors are favourable. The limit of 10 ppm has been conservatively accepted as a safe limit for consumption by infants who are more susceptible to nitrates than are older children and adults. A question we should perhaps ask is: should these sources of water supply be rejected because of an increasing nitrate trend, when the content is still well below the accepted health standard? Does the trend mean that the nitrates will in fact rise above the limit? It can be shown that the use of fertilizer for cash crops will theoretically increase nitrates in groundwater over broad areas of intensively cultivated land by as much as five parts per million, but that level should not rise much higher under prevailing climatic conditions. The level of nitrate in water at a specific sampling point may not establish the content in the water from a heavily pumped well that draws water from a broad area of one or two square miles. Do we really know at what level nitrates significantly affect the health of humans? Can we demonstrate by research how significantly agricultural fertilizer affects groundwater quality? Are we rejecting plentiful supplies of water because of concerns over nitrate buildup and trace amounts of other agricultural chemicals where detailed study may show that this is unnecessary?

3) Landfill Leachate

Leachate is produced in landfills when precipitation percolates through buried solid waste, when waste is deposited below the water table, or when the water table rises into waste because a thick pile of slowly permeable waste alters the local hydrologic regime. Dissolved in landfill leachate are constituents of virtually everything that is in the waste itself and indeed some compounds that are produced by the mixing and interaction of solutes from waste. Leachate is for the most part, produced under anaerobic conditions and has a putrid odour. Because leachate contains many known, and suspected but unknown, water pollutants, great emphasis has been placed recently on the containment of landfill leachate by lining garbage dumps, and attempting with no proven success to cover them so as to restrict infiltration of precipitation. Recognizing that leachate accumulates, it is drawn off and disposed of in waste water treatment plants. Unfortunately, very little hard data exist on how effectively leachate is renovated by conventional secondary waste water practices. We know that BOD is reduced. We know that VOCs are removed; but to where, to the atmosphere? What is the fate of soluble inorganics? They are undoubtedly diluted before release to surface streams, but do they still persist to impact surface water?

Is secondary waste water treatment really superior to the attenuation treatment and dilution that takes place naturally in the soil beneath and around landfills as the leachate is carried slowly by groundwater? We know from experience that leachate contaminated groundwater beneath some very large landfills is renovated by natural processes within a few hundred metres of the landfill. Is this a legitimate use of a small segment of the natural environment? We know the effect will not be permanent. Have we made any quantitative studies to compare the effectiveness of natural subsurface treatment with conventional waste water treatment practices? What are the cost implications? Are we creating problems by making our waste dumps too large? Do we in fact know how seriously leachate affects health? Are there any authentically documented cases to show that waste residues in groundwater affected by landfills have actually made people sick? What evidence have we that artificial containment systems actually stop leachate escape permanently?

In summary, are garbage dumps the alleged monstrous insult to the environment they are thought by many to be, or do they indeed represent a legitimate, temporary use of very small segments of the physical environment? The actual land area used for sanitary landfill is relatively small in spite of the popular contention that we are burying ourselves in our own waste. Have you ever, on a clear day flying for one hour between Montreal and Toronto tried to locate the sanitary landfills? It is difficult, because they are on that scale very small and far between. If we attempted to prove that landfills are a legitimate land use rather than to look microscopically at their adverse effects, might we discover something useful?

4) Soil Classification Criteria For Landfills

In Ontario, disposal criteria have been developed which are designed to control the chemical quality of contaminated soil that, under Ontario Regulation 309 and the Decommissioning Guidelines, must be removed from decommissioned sites. Unfortunately, these rigourous criteria have caused a lot of inert material to be diverted to expensive and already severely burdened sanitary landfills, when much of the material would be perfectly safe if left where it was, or used to "make ground" for useful development. If the soils are classified as registerable waste or subject waste, the transportation and disposal cost in the Toronto region may range from $80.00 to $250.00 per tonne, depending upon the haul distance and character of the material.

The definition of inert fill is so broad that what constitutes inert is often a matter of opinion. Operators of "clean fill" sites are frequently unwilling to accept material if there is doubt as to its origin or chemical content. As a result, sites for disposal of marginally contaminated soil are very scarce.

Prior to acceptance by a municipal landfill, chemically contaminated soil of the type described above must be classified according to Ontario Regulation 309. The Regulation 309 classification procedure involves an acid leach test and comparison with criteria set out in Schedule 4 of the Regulation. Soils that leach less than 100 times (X) the Schedule 4 criteria are acceptable at a municipal landfill subject to further classification as to whether the soil is non-registerable (<10X the criteria), registerable (10 to 100X the criteria) or inflammable.

In my opinion, key questions that need to be addressed; particularly, for soils that are classified as non-registerable are: Is disposal of such soils at a municipal landfill responsible management of scarce landfill capacity? Certainly, in the Toronto area this is a valid question; particularly, when such soil has not generally been utilized for daily cover but rather incorporated into the waste cells? A possible answer may be that in the short term, revenue from receipt of materials classified as waste is considerably higher than materials received for top cover.

Is the current Regulation 309 leachate extraction procedure a proper method of evaluating disposal options for marginally contaminated soils in southern Ontario where conditions are naturally alkaline and where mono disposal of such soils would seem to be the preferred and most cost effective disposal option?

C10 Oxidation to Remove Trichloroethylene from Soil;
G. Farquhar, University of Waterloo, Waterloo, Ontario

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D1

ION MOBILITY SPECTROMETRY IN ATMOSPHERIC ENVIRONMENTAL MONITORING IN THE US SPACE PROGRAM,

G.A. Eiceman, Department of Chemistry, New Mexico State University, Las Cruces, NM 80003

ABSTRACT

The utilization of chemical instrumentation, originating with military establishments, for monitoring atmospheric environmental quality in domestic and space applications represent a little known and potentially rewarding example of technology transfer. Human exposure to hazardous airborne organic vapors at trace levels presents challenges in areas of risk assessment, toxicology, and technology of chemical sensing. Since ca. 1965, improvements in laboratory tools for measuring contamination have kindled interest in health effects from exposures that previously were disregarded. Still, refinements in toxicology, risk assessment, and human protection in those instances were dangers are certain have been hindered by limitations in chemical analysis of environmental and biological samples. While extraordinarily advanced tools for chemical characterization of samples are available, the expense and associated mechanical or electrical requirements of such instruments preclude uses in routine or continuous manner. As a result, the philosophy of environmental analysis has remained stagnant for the last two decades in spite of impressive sophistication of chemical instrumentation. A shift toward continuous monitoring or at least small portable chemical instrumentation is necessary and has been hindered only by the inherent properties and behavior of available technologies for chemical sensing.

Ion mobility spectrometry (IMS) is a derivative technology of a family of ionization detector based upon the conversion of hazardous vapors to ions in air at atmospheric pressure. In IMS, the ions are largely intact, though ionized, molecular species that can be analyzed for speed of movement in a weak electric field. This speed or ion mobility provides a measure of individual chemical constituents through the relationship of size-to-charge rather than mass-to-charge used throughout mass spectrometry. Thus, IMS can be viewed as an advanced smoke alarm where the ionization of atmospheric contaminants is followed by a rapid determination of the physical or chemical characteristics of the same ions. Advantages to IMS, in principal, include small size, low power, and trace detection limits but these were not realized until 1985.

Early developments of modern IMS can be dated to ca. 1965 when a military contract resulted in prototype hardware designs. Commercial versions were publicized in 1970 and several research groups, each with a particular developmental or investigative emphasis. Despite the demonstrated favorable response of IMS toward an impressive range of chemical classes, IMS was regarded widely as potentially significant but with serious limitations in selectivity and reliability. Studies during the last decade have shown these reservations to be rooted in the particulars of mechanisms of ion formation at atmospheric pressure rather than in ion mobility measurements.

Extensive in the consideration of IMS for environmental monitoring was the decision by the US and UK defense establishments to refine IMS for chemical warfare agent detection on battlefields. Ramifications in the use of instrumentation, formerly considered delicate and cumbersome, in such a hostile environmental included rugged, simple, and hand-held designs with refined ionization chemistry for integrity of response. In short, IMS was converted from a laboratory tool to a field monitor in a manner unlike any previous chemical analyzer. Present estimates of military distribution suggest an expansive role for IMS in armies of most western governments.

Instrumentation worthy of combat environments provided an impetus to explore civilian applications and in two instances found niches in the US space program. These two applications that are currently in testing or developmental stages include screening for vapors of hydrazines in the shuttle air lock and the use of portable gas chromatography/ion mobility spectrometry (GC/IMS) as a total hydrocarbon monitor for ambient air. In each instance, a fundamental obstacle to the utilization of IMS as envisioned and the primary emphasis of our research program has been the description and refinement of the chemistry of ionization. These will be discussed as used for the effective transfer of military IMS to environmental monitoring.

E1 Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market; B. Hull, The Conference Board of Canada, Ottawa, Ontario

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P1

UTILIZATION OF ENVIRONMENTAL RESEARCH TO CONTROL LEAD CONTAMINATION

by

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U.S.A.

ABSTRACT

Due to the lack of well founded guidelines in the United States and other countries for lead contamination in soil, a special Society for Environmental Geochemistry and Health (SEGH) task force was formed to utilize research data and actual case studies to develop a report on recommended guidelines for Lead in Soil. An action oriented plan on how to systematically evaluate lead contamination for the protection of public health or determine lead levels to be used for remedial actions will be presented with examples of how to determine action levels for control or remedial measures associated with lead contamination problems.

INTRODUCTION

Technology transfer is a scientific terminology that implies many different interpretations dependent upon how it is used. In the United States, the Federal Technology Transfer Act (FTTA) of 1986 was passed to help remove perceived barriers for collaboration and utilization of research between the public-private sector. The preamble to the FTTA bill also noted that "many new discoveries in science occur at universities and federal laboratories while the application of this knowledge depends upon industry." (Nichols, 1990). However, technology transfer is often easier to propose than to implement due to the following constraints:

1. Cultural resistance encountered within countries and specific locations.
2. Time requirements before profit payback.
3. Necessity to also transfer appropriate training to carry out new technology.
4. Uncertainties of legal or regulatory requirements.

Our present time of environmental awareness has received further intensification by current environmental crises (such as the Alaskan oil spill, etc.), so that the public demands a more rapid transition of environmental research methodologies into practical applications. One major difficulty is how to evaluate research and transfer selected laboratory or field methodologies as rapidly as possible into a new or improved technology. For example, in Canada, the proposed process of converting sewage sludge into fuel, has the potential of replacing over 700,000 barrels of oil at a possible savings of over $28 Million at present oil prices which may continue to increase in the present unstable geopolitical mideast crisis (Nichols, 1990). While this may serve as a good model to illustrate technology transfer, industry is often reluctant to invest in many processes because of the difficulty in receiving government approval for the technology proposed. Environmental research may also be utilized for the development of guidelines such as the control of lead contamination and allow for the use of appropriate technology, including remedial actions, to be approved by public health officials and regulatory agencies for use by concerned industries.

USE OF ENVIRONMENTAL RESEARCH

The absence of scientifically recognized guidelines in the United States, as well as other countries, concerning the acceptable concentration of lead in soil (Davies and Wixson, 1987) has contributed to confusion by regulatory agencies, industries, public health officials, the medical community and concerned citizens (Lead in Soil, 1988). The questions most often asked focus on possible adverse health effects and risks from lead exposure or the recommended permissible soil lead concentration to be used for remedial action at contaminated or hazardous waste sites (Davies and Wixson, 1986).

Preventive measures or control technologies are usually not applied when there is an uncertainty of regulatory requirements. Therefore, environmental research data from around the world was utilized by a Society for Environmental Geochemistry and Health (SEGH) task force in developing a report on recommended guidelines for "Lead in Soil" (Wixson, 1988). This report illustrates how cooperative efforts between industries and regulatory officials may be applied to determine the risk of human exposure to lead (Davies and Wixson, 1989). The methodology used in this report also shows how environmental research can be applied to develop guidelines necessary for the application or control of remedial technologies.

The SEGH task force was formed in 1988 to address the problems, evaluate data and develop scientific recommendations concerning lead in soil. The risk assessment steps of: 1) hazard identification; 2) dose-response assessment; 3) exposure assessment; and 4) risk characterization were used develop a "Phased Action Plan" (illustrated in Figure 1) which evaluates the relationship between blood lead levels and the levels of lead in soil as one possible source of exposure. The "Phased Action Plan" also required extensive review of research data and case studies for the development of a target soil lead/dust lead guideline model derived from the use of documented health criteria.

The factors associated with Lead and Health are concerned with the population groups at risk from the possible adverse health

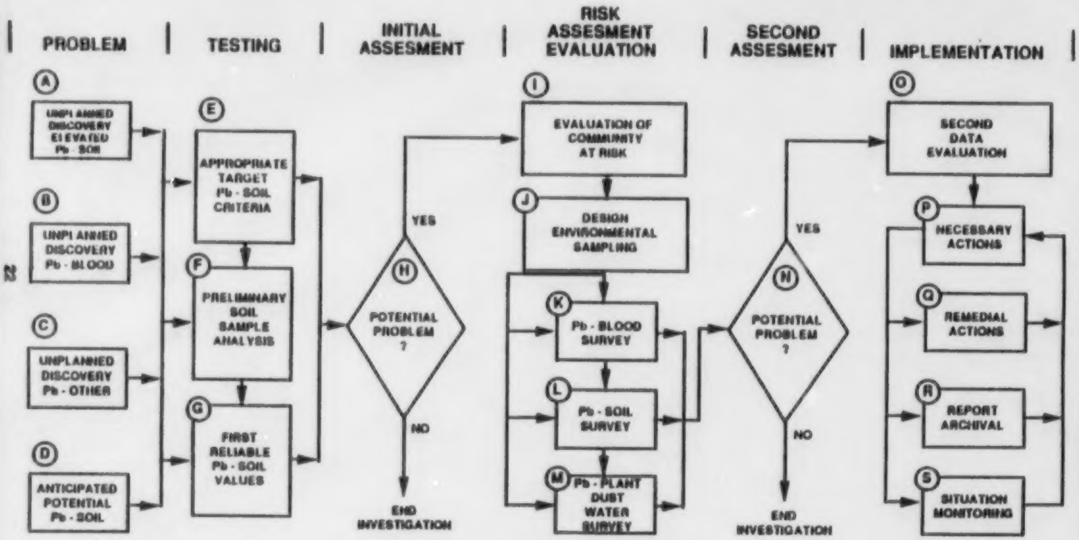
PROBLEM
TESTING
INITIAL ASSESMENT
RISK ASSESMENT EVALUATION
SECOND ASSESMENT
IMPLEMENTATION
Ⓐ UNPLANNED DISCOVERY ELEVATED Pb - SOIL
Ⓑ UNPLANNED DISCOVERY Pb - BLOOD
Ⓒ UNPLANNED DISCOVERY Pb - OTHER
Ⓓ ANTICIPATED POTENTIAL Pb - SOIL
Ⓔ APPROPRIATE TARGET Pb - SOIL CRITERIA
Ⓕ PRELIMINARY SOIL SAMPLE ANALYSIS
Ⓖ FIRST RELIABLE Pb - SOIL VALUES
Ⓗ POTENTIAL PROBLEM ?
YES
NO
END INVESTIGATION
Ⓘ EVALUATION OF COMMUNITY AT RISK
Ⓙ DESIGN ENVIRONMENTAL SAMPLING
Ⓚ Pb - BLOOD SURVEY
Ⓛ Pb - SOIL SURVEY
Ⓜ Pb - PLANT DUST WATER SURVEY
Ⓝ POTENTIAL PROBLEM ?
YES
NO
END INVESTIGATION
Ⓞ SECOND DATA EVALUATION
Ⓟ NECESSARY ACTIONS
Ⓠ REMEDIAL ACTIONS
Ⓡ REPORT ARCHIVAL
Ⓢ SITUATION MONITORING

Figure 1. Phased action plan for lead in soil

effects of lead. Therefore, health criteria and research data were used in deriving a target soil/dust lead guideline concentration.

A single number for a lead in soil guideline for the protection of young children was considered unrealistic for a number of reasons. The population at risk can itself vary; therefore, the soil/dust guideline was established as a relationship or formula, in order to allow for a variety of environmental situations and regulatory criteria.

In the model developed, blood lead concentration was equated to a baseline level plus an increment resulting from exposure to soil or dust lead. The model also takes account of the chosen blood lead guideline or target concentration and the degree of protection requred for the population. The slope of the blood lead-soil lead relationship is then used in calculating an increase in blood lead over a baseline value. Hence the soil guideline, can vary depending on a variety of factors, allowing this response to be adjusted for a given situation with the opportunity of being modified as more research data become available.

The derivation of the blood lead/soil lead model is illustrated in Figure 2.

The major uncertainty in the use of such a realtionship is the value to use for δ , the response of blood lead to increasing soil or dust lead concentration. It therefore appears that a value in the range of 2-5 would be appropriate for most siutations and that the major influence on a value for δ may in fact be child activity rather than any characteristics of dust or soil.

RISK MANAGEMENT

The risk management section of the SEGH report emphasizes the exposure assessment and development of a relationship between blood lead levels and the concentration of lead in soil to formulate suggested guidance for acceptable soil lead. Geographic and physical processes that affect soil lead accumulation are discussed along with social aspects of lead contamination and other risks.

Legal aspects and cleanup levels for lead are presented along with economic considerations of appropriate technology utilized for remedial actions.

SUMMARY

The lack of guidelines or regulations often contribute to difficulties in implementation of improved technology for the control of metal contamination. The use of environmental and human health research data coupled with case studies of lead contamination have been used by a SEGH task force to develop a

TARGET SOIL/DUST LEAD GUIDELINE MODEL
DERIVED FROM USE OF HEALTH CRITERIA

$$S = \frac{\left| \frac{T}{G^n} - B \right|}{\delta} \cdot 1000$$

where:

S is the soil or dust guideline, a geometric mean concentration in μg Pb per gram of dust (ppm)

T is the blood lead guideline or target concentration, in μg Pb/dl whole blood

G is the geometric standard deviation of the blood lead distribution, typically in the range of 1.3 to 1.5

B is the background or baseline blood lead concentration in the population from sources other than soil and dust

n is the number of standard deviations corresponding to the degree of protection required for the population at risk, and would normally follow from the way in which the blood lead guideline T was defined

δ is the slope or response of the blood lead - soil(dust) lead relationship and has the units of μg Pb/dl blood increase per 1000 ppm increment of soil or dust lead

Figure 2.

Derivation of the blood lead/soil lead model report on recommended guidelines for lead in soil. These guidelines are necessary to control of lead contamination by recommending action levels to protect public health. Recommended levels of lead contamination in soil also may be used to determine how clean is clean? when remedial action is necessary.

ACKNOWLEDGEMENTS

The support of the Society for Environmental Geochemistry and Health, the International Lead Zinc Research Organization, Inc., the Lead Industries Association and the US Environmental Protection Agency is acknowledged. Special thanks also to the members of the Lead in Soil task force for their time and effort on this important project.

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VOLUME I

PANEL PRESENTATIONS

P1

"GLOBAL WARMING: WHAT IS AT STAKE?

THE INTERNATIONAL SCENE: J. P. Bruce

With the first assessment report of the Intergovernmental Panel on Climate Change (IPCC), and the Second World Climate Conference (SWCC) completed, discussion of greenhouse gases and climate change are now moving to a more formal stage of international negotiation of a Convention on Climate Change. The positions taken by various countries at the IPCC meetings and the debates at the SWCC give clear indications of some of the major issues that will have to be addressed in negotiation of a global Convention. These issues will be identified and some possible means will be suggested of addressing the diverse concerns.

Major changes in both environmental and economic policies, especially in the energy sector, will be needed in most countries if an effective international agreement is to be reached.

P2

GLOBAL WARMING: A CANADIAN PERSPECTIVE AND ACTION STRATEGY

Dr. D. Kirk Dawson
Director General
Canadian Climate Centre

Climate Change is perhaps one of the best examples of global interdependence of countries. An effective response will require a global effort which is likely to have considerable impact on human kind. A major dilemma, however, is that actions may be required well before many of the specific issues can be analyzed more thoroughly by further research.

Some of the more stringent actions that may be required, particularly those which serve to limit emissions of greenhouse gases, will have a profound effect on national policies in all areas. The manner in which nations address this issue will have major implications for trade and economic balance, between industrialized and developing countries, between industrialized nations themselves and within the different regions of individual countries.

Canada has played a significant role in seeking international solutions. We have been an active participant on the Intergovernmental Panel on Climate Change (IPCC) and are strong proponents of the negotiation of a comprehensive global convention on climate change.

At home, Canada supports a world-class climate research and impacts program and is now working with the provinces to conclude a National Action Strategy on climate change. The strategy will be:

- Comprehensive. It will deal with all of the major sources of greenhouse gases and the sinks of those gases;

- National in Scope. It will contain strategies appropriate for all levels of government, as well as industry and individuals, while recognizing that climate change is a global problem requiring international cooperation; and

- Action-oriented. It will be a cost effective and flexible action program that is based so that it can respond to new understanding and developments in the future.

P3

Global Warming: What Is At Stake?
Socio-economics

Erik Haites

In relation to global warming, socio-economics could cover many issues. To meet my time constraints, I must limit the scope of my presentation.

I will not discuss the socio-economic consequences of global warming, nor the socio-economic implications of adaptation to climate change. For Ontario, these were reviewed at a workshop organized by the A.E.S. in November 1985. A summary of that workshop is available in the Climate Change Digest (CCD 88-08) "CO_2 Induced Climate Change in Ontario: Interdependencies and Resource Strategies."

Today, I will focus on two socio-economic aspects of global warming that are the subject of more current research. They are:

- the costs of achieving reductions in emissions of greenhouse gases, and
- the potential application of economic instruments to reduce greenhouse gas emissions.

Following the Toronto Climate Conference in June 1988, analysts started to examine how the proposed interim target of a 20% reduction in 1988 emissions of CO_2 by 2005 could be achieved. I reported on such an analysis for Canada at this conference last year. During 1989 and early 1990, studies were completed for a number of countries. The universal conclusion is that the Toronto Conference target is a tough one. Virtually, all currently available CO_2 emissions abatement measures will need to be implemented to their full technical potential to reach that goal.

Once the measures needed to achieve the target are known, people want to know the cost of implementing those measures. Although some preliminary answers are available, this is a matter that is currently under intense study.

The preliminary cost estimates range from about -0.3 to +0.5 percent of GNP annually to 2005. Some studies show net savings, as a result of lower energy consumption, from measures to reduce emissions of CO_2. Other studies show a net cost for these measures. The results tend to vary systematically with the methodology used.

Typically, energy efficiency, measures account for the bulk of the CO_2 emissions reductions to 2005. Studies that analyse the economics of individual energy efficiency measures, find most of these measures to be attractive from a societal perspective. They assume that the measures are implemented as part of the normal replacement cycle. This yields an overall saving as a result of implementing the CO_2 emissions reduction measures. Studies for Canada and Australia are good examples of this approach.

The other approach to estimating the cost of CO_2 emissions abatement is to use a macro-economic model. A carbon tax is used to achieve the target reduction in emissions. The tax revenues are recycled so that there is no net loss to the economy. Studies of this sort for the U.S., Japan, and other countries, all yield positive costs for CO_2 emissions reduction.

The carbon tax approach causes all energy users to adjust their energy consumption and equipment at the same time, reflecting the introduction of the tax. Adjustments do not reflect the replacement cycle for energy using equipment, thus raising the adjustment costs. On the other hand, assuming that all adjustments occur as part of the normal replacement cycle and that the adjustment costs of the equipment producing industries are reflected in the equipment prices, undoubtedly understates the adjustments. There are probably other reasons as well for the differences in the cost estimates produced by the two methodologies.

In any event, the first order estimates of the cost are between -0.3 and +0.5 percent of GNP. Research currently underway will refine these estimates and provide a better understanding of the nature and magnitude of the costs.

Economists believe that policies, such as emissions charges or tradeable emissions permits, can achieve a specified environmental target at lower overall cost than emissions regulations. Given the scale of the emissions reductions proposed by the Toronto Conference target, cost-effective policies are doubly important. I stressed the need for such policies in last year's session.

Tom Tietenberg and I have outlined a linked system of emissions permits and emissions taxes for carbon dioxide and other greenhouse gases. Briefly, the system is as follows. Each country is assigned emissions targets by international agreement; developing countries would probably have targets greater than current emissions and developed countries might have targets 25 percent below current emissions.

Within a country, such as Canada, large sources could earn permits for reductions beyond their target. Other large sources, such as industries, electric utilities, and large commercial and institutional facilities, could purchase permits in order to reach their target reduction. The fuels used by smaller sources, residences, vehicles, and small commercial facilities, would include an emissions tax equal to the market price of the permits. Thus, all sources have the same target reduction and the same cost per unit of CO_2 reduced.

International trade in permits would be allowed. However, each country could establish import and export restrictions. Developing countries could restrict trades between subsidiaries and parent companies if they chose. A country could restrict imports from countries whose permits it judged to be of dubious value. These arrangements provide economic incentives to participate in the international agreements for control of greenhouse gases. And, they provide enforcement mechanisms without requiring an international inspectorate.

The system, we believe, could be extended to CFCs, many sources of methane emissions and afforestation, but not to nitrous oxide, ozone, or ground level ozone precursors.

In conclusion, policy analysis of global warming is proceeding at a very rapid pace. Last year, the potential abatement measures and the scale of the response required were just being determined. They are now fairly well known and preliminary estimates of the associated costs are available. These cost estimates are being refined and appropriate policies are being formulated. Next year, I hope that we will know what policies are to be implemented in Ontario, in Canada, and internationally.

P4

WARMING TO A CRISIS:
THE MEDIA AND CLIMATE CHANGE

Abstract for a speech

By Michael Keating
Environment Writer and Consultant

to

The Technology Transfer Conference of Environment Ontario
Royal York Hotel
November 20, 1990

Global warming hit the front pages in Canada in October, 1983. This came immediately after the New York Times broke the story of the EPA report by John Hoffman, saying the greenhouse effect would begin in the 1990s.

This led to a small flurry of stories, which grew slowly but steadily into a trickle, and, over the last few years, into a flood.

The pace of coverage picked up in the mid-1980s as more of the big media, such as Time Magazine and the TV networks, caught on to climate change as a mega-story. There was talk of a threat to human life.

It was and is a great story for graphic images. Belching smokestacks and burning forests. Kentucky winters in Toronto. Glaciers crashing into the sea as the ice caps melt. Waves lapping at the doors of Wall Street. Two, three or four Prince Edward Islands. Florida going back the the alligators. Hurricanes with 40 to 50 per cent more punch than now.

People even coined the term "heat beat" for reporting on climate change.

The story got a real boost in 1988 when reporters had both the devastating heat waves in central North America and the Toronto conference on the changing atmosphere. And that was when James Hansen of NASA told the U.S. Congress that he was 99 per cent sure that climate change had begun.

The seriousness of the issue was reinforced by the record drop in the Mississippi River and ensuing calls from some U.S. politicians for water diversions from the Great Lakes.

So, how have the media covered the science of global warming?

Since the early 1980s, reporters have generally accepted that climate change is a real and poses a serious threat. They have given relatively little coverage to scientists, or politicians, who say this is just a theory.

I think reporters feel global warming is a fairly easy concept to grasp. Humans put billions of tonnes of gases into the atmosphere. Billions is a big number, so it must have an impact.

Reporters have generally treated climate change as a "bad thing" but that has not been universal. There are still some stories about the benefits of warmer winters and less snow.

How responsible have the news media been in reporting on global warming? By and large the reporting that I have seen has been fairly accurate. It has been much better than coverage of some issue such as PCBs.

But whether or not you like the coverage so far depends a lot on what hat you are wearing.

If you are a scientist who believes that global warming is a problem, then you are probably happy with the fact the media have made the greenhouse effect as common a phrase as acid rain. I think the environment movement feels the same way.

If you are a scientist who believes it is just a theory, then you probably feel the media have not been critical enough of the other scientific camp.

If you a minister of environment and have been in the portfolio long enough to understand the issues, then you probably like the coverage. You will hope that the media put more pressure on the premier or prime minister and the minister of energy to come up with greenhouse gas strategies.

If you are the minister of energy you probably wish the media would stick to covering the deficit or the ups and downs of the stock market.

If you work for the oil and coal industry you probably don't want to open your paper in the morning.

Where will news coverage go in the future?

The media are on to the fact that, per capita, Canadians are the world's greatest energy users and one of the world's greatest producers of greenhouse gases.

Where will the mud from this kind of coverage stick?

That's very hard to predict. A lot depends on the critics and on scientific research that is released to the public.

We have already seen considerable criticism of the coal-burning power plant at Point Aconi, Cape Breton, and some criticism of Hibernia in the east, and heavy oil projects in the north, because of they will all add CO_2 to the atmosphere.

There is an increasing number of stories about CO_2 from automobiles but the media have an ambivalent role in this one, since most reporters drive cars, and the media get a lot of revenue from auto ads.

The media face at least two difficult tasks ahead.

One will be in deciding when to report that global warming has started. The second will be in focussing on what to do about the problems.

Expert groups, including the Toronto atmosphere conference, suggested that the world should start switching to low or no carbon fuels such as hydro-electricity, wind, solar power, natural gas, biomass and possibly nuclear energy, if it can be made safe and if its use does not lead to more nuclear weapons.

We are also hearing calls from less developed nations for massive assistance to help them cut or avoid the emission of greenhouse gases while reducing poverty, hunger and disease.

These are complex stories, often without a clear set of targets to shoot at. Reporters are going to need lots of help from the scientists, policy makers, researchers, environment groups and others.

I remember quoting the Brundtland Report as saying we need lifestyles that are, "within the planet's ecological means." And I remember asking Maurice Strong if humans can make that kind of shift quickly enough. He said, "it is going to be a race between our sense of survival and our more indulgent drives."

What we need now is articulate spokespersons who will tell the public, through the media, how we are going to win that race.

* * *

P5

1990 TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 20, 1990

ABSTRACT OF J.D. McFARLAND'S REMARKS

The potential for global warming has become one of the most complex and hotly-debated issues in the energy/environment dialogue. Although there appears to be an emerging scientific consensus that an enhanced greenhouse effect is real, many uncertainties remain with regard to the magnitude, timing and regional effects. Canadians as yet do not fully understand the implications of this issue on public policy development nor the economic consequences of potential policy measures to address it. The energy industry is vitally concerned about promoting sound public policy in this area, and Imperial Oil has been active in providing a perspective on the issue in the context of domestic and international energy use. Imperial's initiatives to generate a broader understanding of the scientific and economic implications for Canada and Imperial are discussed.

J.D. McFarland/wl
October 5, 1990

P6

Global Warming: What's Known and What's Not?

Bunli Yang

Global warming and what industrialized societies might do about it have become topics of intense debate. Apart from its importance as an environmental issue, and it is often regarded the most serious threat to the global environment, global warming has many uncertainties. That kind of uncertainty generates debate and may be a barrier to action.

It is straightforward to list what is known about global warming and climate change:

- there is a natural greenhouse effect in our atmosphere because of gases that trap heat;
- the natural greenhouse effect accounts for a warming of about 33 C.;
- the climate of an ice age differed from today's by a small change in average temperature, about 5 C.;
- in the past, average temperatures and concentrations of the greenhouse gases have been high together and low together;
- human activities have been increasing the concentrations of the greenhouse gases in the atmosphere;
- the impacts on climate of rapid changes in temperature will not be uniform;
- climate is inherently global, and international agreement on actions will be very difficult.

The list of unknowns is, of course, endless. They range from the phsyical science of clouds and oceans to the economics and the social impacts of climate change. Examples are the rise in sea level for any level of greenhouse gas concentrations, or the rate of temperature rise, or the amount of precipitation and soil dryness because of any warming, or the costs of prevention, or the costs of adaptation to climate change. The risks of climate change, though not known or even knowable, are widely regarded to be major.

While these unknowns may loom large, uncertainties about usual economic trends are even larger, but are not barriers to economic policies and actions.

For purposes of public policy, the relevant question is not "How much needs to be known with high certainty before taking action?" but "What should be done now, by whom, in the face of the risks?"

VOLUME I

SESSION A

AIR QUALITY RESEARCH

VERBAL PRESENTATIONS

A2

Genetic Characteristics of Healthy and Declining Sugar Maple (*Acer saccharum* Marsh.) in Ontario

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P7B 5E1

Over the past few years forest decline has attracted global concern (Schutt and Cowling, 1985; Knight, 1987) with the changing chemical climate proposed as a probable contributing factor (Anderson, 1989; Schulze, 1989) in combination with an interaction of other stress factors. Among Canadian species, sugar maple (*Acer saccharum* Marsh.) has elicited the greatest concern with reports of decline in Ontario as early as 1947 (McIlveen *et al.*, 1986). Causal factors remain obscure with indications suggesting that acidic precipitation as but one more stress in addition to those of insect outbreaks and drought (Hendershot and Jones, 1989; Linzon, 1986; McLaughlin *et al.*, 1985).

Previous research in pollution and forest trees has provided reason to believe that genetic differences may exist between healthy and declining individuals (*e.g.*, Kriebel and Leben, 1981; Scholz and Venne, 1989). Thus, concern about the potential erosion of genetic resources through the elimination of sensitive individuals has been expressed (Karnosky *et al.*, 1989; Scholz, 1981). The purpose of the present study was to determine whether possible genetic differences between healthy and declining sugar maple within the same sites are discernable at the allozyme level. Regardless of the specific causal agents, the determination of any link between genetic markers and visible injury could provide a foundation for selection and management decisions.

MATERIALS AND METHODS

Four sites previously selected as part of the Ministry of the Environment studies (Beak Consultants Ltd., 1989) were chosen with two near Dorset, Ontario (named Boothby and L.M. Frost) and two near Peterborough, Ontario (called Brackenridge and Davies). At each site bud tissue was collected from each of 24 trees previously classed as healthy and about 24 classed as declining, totaling to a sample size of about 48 trees per site. A decline index (DI) was available for each tree based on percentages of dead branches, chlorosis, and undersized leaves (McIlveen and McLaughlin, 1988). Bud tissue was prepared and starch gel electrophoresis was conducted as previously described (Perry and Knowles, 1989). Only variable loci (eleven in total) among nine enzyme systems were assayed as follows: aspartate aminotransferase (*Aat*), aldolase (*Ald*), diaphorase (*Dia*), leucine-amino-peptidase (*Lap*), malate dehydrogenase (*Mdh*), 6-phosphogluconic dehydrogenase (*6pg*), phosphoglucose isomerase (*Pgi*), phosphoglucomutase (*Pgm*), superoxide dismutase (*Sod*).

Allele frequencies were estimated for both subsamples of each population based on observed genotypic arrays and allelic heterogeneity was assessed using standard non-parametric chi-square tests. Due to overlap of DI scores within some sites, healthy and declining subsamples were defined as the trees with the lowest 20 and highest 20 DI scores within each site when scores were ordered sequentially within site.

Expected heterozygosities (H_e) were estimated for each locus within each subsample as:

$$H_e = 1 - \Sigma p_i^2,$$

where p_i was the estimated frequency of the *i*th allele at the locus. A measure of the deviation of observed heterozygote frequency from that expected under Hardy-Weinberg equilibrium, F_{IS}, was calculated for each subsample as:

$$F_{IS} = 1 - H_o/H_e,$$

where H_o was the observed proportion of heterozygotes. The contribution of each locus to a subsample's mean F_{IS} was weighted by its expected heterozygosity in that subsample. Values of F_{IS} greater than 0 indicate an excess of homozygous genotypes relative to Hardy-Weinberg expectations while negative values are indicative of an excess of heterozygotes. For each site subsample differences in means of H_e, H_o, and F_{IS} were evaluated using paired *t*-tests.

The possibility of a relationship between heterozygosity and vigour was explored through a regression analysis of individual tree data. The independent variable was the proportion of loci heterozygous in a tree and the dependent variable was the tree's DI. This analysis was performed for each site using the computer program MCREG of BIOSTAT I (Pimentel and Smith, 1985).

RESULTS

Observed allele frequencies of the healthy and declining subsamples within the four sites are presented in Table 1. Allelic heterogeneity tests indicated significance (*P*=0.04) at *Mdh-3* in

TABLE 1. ALLELE FREQUENCIES OF HEALTHY (H) AND DECLINING (D) SUGAR MAPLE AT FOUR SITES (ORIGINAL DATA).

		SITE[1]							
		BOTH		BRAK		DAV		LMF	
LOCUS	ALLELE	H	D	H	D	H	D	H	D
Aat-1	1	0.98	0.94	0.99	0.96	1.00	0.93	1.00	0.95
	2	0.02	0.02	0.01	0.04	0.00	0.00	0.00	0.02
	3	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.03
	4	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
Aat-2	1	0.69	0.85	0.67	0.73	0.98	0.79	0.79	0.83
	2	0.31	0.15	0.31	0.25	0.00	0.21	0.21	0.17
	3	0.00	0.00	0.02	0.02	0.02	0.00	0.00	0.00
Ald-3	1	0.90	0.89	0.98	0.90	1.00	0.92	0.95	0.94
	2	0.10	0.00	0.02	0.10	0.00	0.08	0.00	0.00
	3	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.06
	4	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Dia-3	1	0.88	0.96	0.96	0.92	0.96	0.92	0.85	0.92
	2	0.08	0.04	0.04	0.08	0.04	0.08	0.13	0.08
	3	0.04	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Lap-1	1	0.98	0.98	1.00	0.94	1.00	1.00	1.00	1.00
	2	0.02	0.02	0.00	0.06	0.00	0.00	0.00	0.00
Lap-2	1	0.96	1.00	0.98	0.98	1.00	1.00	1.00	0.95
	2	0.04	0.00	0.02	0.02	0.00	0.00	0.00	0.05
Mdh-3	1	0.95	1.00	0.94	0.88	0.98	0.85*	0.90	0.90
	2	0.05	0.00	0.06	0.04	0.02	0.15	0.04	0.05
	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
6pg-1	1	1.00	1.00	0.98	1.00	1.00	0.96	0.96	1.00
	2	0.00	0.00	0.02	0.00	0.00	0.04	0.04	0.00
Pgi-2	1	0.88	0.75	0.73	0.79	0.73	0.67	0.83	0.79
	2	0.08	0.17	0.21	0.19	0.08	0.15	0.13	0.10
	3	0.04	0.04	0.02	0.00	0.15	0.06	0.02	0.04
	4	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
	5	0.00	0.02	0.02	0.02	0.04	0.13	0.00	0.06
Pgm-1	1	0.90	0.91	0.96	0.90	0.81	0.88	0.90	0.88
	2	0.00	0.02	0.02	0.02	0.02	0.04	0.04	0.00
	3	0.10	0.07	0.02	0.08	0.17	0.08	0.06	0.13
Pgm-2	1	0.98	1.00	1.00	0.96	1.00	0.96	1.00	0.96
	2	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.02
	3	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.02

[1] Site names: BOTH=Boothby; BRAK=Breckenbridge; DAV=Davies; LMF=L.M. Frost.

*Significant (P<0.05) difference between subsample allele frequencies within site.

Davies site only. Paired t-tests indicated a significant difference in the levels of expected heterozygosity of the healthy and declining subsamples within the Davies site with the declining subsample having a greater mean H_e (Table 2). However, in the remaining sites H_e was usually larger, but not significantly so, in the healthy subsamples. No significant trend was observed concerning a possible relationship between DI and observed heterozygosity and none of the sites demonstrated significant heterogeneity of mean H_o among subsamples (Table 2). A consistently greater F_{IS} was noted in the declining subsamples relative to the corresponding healthy subsamples (Table 2). Although paired t-tests did not find any of these observed differences within sites to be statistically significant, the apparent trend is compelling.

Not unexpectedly, the results of the regression analysis reflected the observations made of H_o above. The possibility of a relationship between heterozygosity and state of decline was strongest in the Davies site with a correlation (r) between individual heterozygosity and DI of 0.27 (P=0.06). The Boothby, Brackenridge and L.M. Frost sites had r values of -0.22 (P=0.13), -0.21 (P=0.16), and 0.05 (P=0.74) respectively. Clearly, there was no consistent trend.

TABLE 2. EXPECTED (H_e) AND OBSERVED (H_o) HETEROZYGOSITIES AND FIXATION INDICES (F_{IS}) OF HEALTHY AND DECLINING SUGAR MAPLE AT FOUR SITES

	HEALTHY			DECLINING		
SITE[a]	H_e	H_o	F_{IS}	H_e	H_o	F_{IS}
Both	0.18	0.19	-0.080	0.14	0.14	-0.030
Brak	0.17	0.19	-0.100	0.18	0.18	0.000
Dav	0.13	0.13	-0.008	0.18[b]	0.17	0.101
LMF	0.15	0.15	-0.008	0.15	0.15	-0.030
Pooled Data	0.16	0.17	-0.044	0.16	0.15	0.060

[a] See Table 1 for meaning of abbreviations.
[b] Estimates differ significantly (P<0.05) between subsamples within site.

DISCUSSION

Several observations made in the course of this study are of interest. First, where some others report increased heterozygosity in forest trees tolerant of environmental stress (Geburek *et al.*, 1987; Muller-Starck, 1985, 1989) we found no evidence of such a trend either in comparison of mean heterozygosity measures of subsamples or in the regression analyses. The only statistically significant relationship observed was contradictory with a greater mean H_e found in the declining subsample of the Davies site, but not observed in data of the other sites.

The Davies site was also unique in that significant allelic heterogeneity was observed among its subsamples for a single locus, *Mdh-3*. Such allelic heterogeneity has been observed in other studies (*e.g.*, Bergmann and Scholz, 1985) and implicated by researchers to be involved in resistance mechanisms. Since the distribution of allele 2 at *Mdh-3* in the Boothby site is opposite to that at the Davies site, we doubt that this locus is directly involved with a resistance mechanism or is a specific target of selection.

Differences in allele frequencies between tolerant and sensitive phenotypes in this and similar allozyme investigations could be accounted for by influences other than selection imposed by environmental stress. For example, the cohort structure (progeny produced during the same year) may be genetically differentiated (Mulcahy, 1975) potentially influencing the population's genetic architecture. Furthermore, differential disturbance such as soil compaction by livestock and sap collection may damage trees independent of genotype.

What inferences can be drawn from our findings? Perhaps the most notable trend observed was that of the mean F_{IS}. In spite of the fact that differences in mean F_{IS} between healthy and declining populations did not attain statistical significance, the fact that all four populations displayed greater F_{IS} in declining subsamples suggests to us that the perceived trend is something more than an ephemeral aberration. This trend indicates that the proportion of heterozygous loci per individual relative to Hardy-Weinberg expectations tends to be greater in the healthy individuals. Such a condition could occur if the more inbred individuals are predisposed to decline, or if heterozygosity in general confers resistance to decline or both. It is difficult to distinguish between these two possibilities (Mitton and Jeffers, 1989). That the significant difference in heterozygosities observed among subsamples at the Davies site had the declining subsample with the highest heterozygosity would suggest that heterozygosity *per se* does not necessarily impart resistance.

This investigation raises many new questions. Is there variation in the level of decline among cohorts within sites? What is influencing the different genetic trends among sites? For example, does the absence of a convincing genetic trend between healthy and declining subsamples among sites indicate that the allozyme procedure is inadequate or that the stresses are complex affecting trees and sites differentially? As is the case with the study of interactions of environmental stress and genetic components in general, the problems involved in the investigation of the association of genetic parameters and the maple dieback are multifarious.

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A3

Preliminary Report: Interpretation of Sugar Maple (*Acer saccharum*) Ring Chronologies from Central and Southern Ontario using a Mixed Linear Model

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1. Introduction

Recent declines in the growth rate of tree species, such as Jeffrey pine (*Pinus jeffreyi*) (Peterson *et al.* 1987), loblolly pine (*Pinus taeda*) (Zahner *et al.* 1989), Norway spruce (*Picea abies*) (LeBlanc *et al.* 1987), red pine (*Pinus resinosa*) (LeBlanc *et al.* 1987), red spruce (*Picea rubens*) (Adams *et al.* 1985, Cook 1988, Ord and Derr 1988, Van Deusen 1987, Zedaker *et al.* 1987), Scots pine (*Pinus sylvestris*) (Kullman 1987, LeBlanc *et al.* 1987), and white oak (*Quercus alba*) (Phipps and Whiton 1987), have been extensively documented. The decline has been ascribed to such factors as atmospheric deposition, (LeBlanc *et al.* 1987, Zahner *et al.* 1988), climate changes, (Kullman 1987) and stand dynamics (LeBlanc *et al.* 1987, Van Deusen 1987).

Decline in the growth rate of Sugar Maple (*Acer saccharum*) has been reported as early as 1952 in Ontario and 1963 in Michigan (Mclaughlin *et al.* 1985). In both cases the decline was attributed to other factors such as over cutting, farming activities and heavy insect infestations. Hornbeck *et al.* (1987, as cited in Innes and Cook, 1989) suggest that in the northeast U.S. the decline associated with red pine, has not extended to the Sugar Maple. Conversely Kim (1990) suggests that Sugar maple in the Adirondack Mountains may be affected by atmospheric deposition. Recently in Ontario, observational evidence suggests that the health of larger sugar maples is deteriorating (Mclaughlin *et al.* 1985).

Statistical methods used to investigate the relationship between the decline in growth rate and various natural and anthropogenic factors are in general based on a function which removes trends associated with stand dynamics (detrending function). Such a function may be a growth curve, (Fritts 1976, Sundberg 1974, Van Deusen 1987), an empirical linear model (Van Deusen 1987), a time series model (Harvey 1984, Monserud 1986) or a digital filter (Robertson and Jozsa 1988, Craddock 1957). Upon removal of stand dynamic trends, various multiple regression techniques have been used to determine whether the remaining factors, such as climate, site suitability etc, account for a significant proportion of the variability in the standardized growth ring widths. Fritts (1976) advocates the use of principal components to summarise climatic data. Other simpler approaches utilize the monthly means and one year lagged monthly means of the climatic data.

When all natural factors have been accounted for, the tree-ring chronology is then examined for further trends which may be associated with anthropogenic factors.

Innes and Cook (1989) and Zahner *et al.* (1989) recognize that these methods may be *removing* important information pertinent to the long term trends associated with anthropogenic factors and thus may not be appropriate for investigating these relationships.

The objective of this study is to develop a statistical model which relates growth rates of sugar maples in Central and Southern Ontario to climatic and ecotypic variables. This problem is examined using a data base containing tree-ring chronologies of sugar maples from woodlots in Central and Southern Ontario, obtained from the Ontario Ministry of the Environment. The model will then be used to determine whether there is sufficient evidence to suggest that atmospheric deposition is responsible for a recently observed decline in the growth rate of sugar maple trees in Central and Southern Ontario.

These data were collected observationally. If important factors are omitted from the model, the estimates of the relationship between tree growth and the factors of interest may be biased. In situations such as this, one should be aware that alternative explanations may exist.

2. Description of Sampling Design and Data Collection

2.1 Chronology Data

The Ontario Ministry of the Environment has conducted a field trial to measure the growth rate of sugar maple and relate this to environmental conditions when the growth was taking place.

Three regions were chosen for study: Southwestern Ontario, represented by 5 plots south west of St. Williams (heavy atmospheric deposition), Central Ontario, represented by 5 plots in Barrie, and 18 plots in either the Algonquin Park and the Kawartha area (moderate atmospheric deposition), Western Central Ontario, represented by 18 plots north or east of Sault Ste. Marie (North Shore) (light atmospheric deposition).

Each plot was established using the following criteria. (1) The stand must be at least 10 ha in size. (2) It must be remote from point sources of air pollution ($\geq$ 30 km) or urban centers ($\geq$ 15 km). (3) There should be no major thinnings in last 10 years. (4) A documented stand history should exist. (5) The basal area of the plot should be between 14 and 25 m^2/ha . (6) The average age of trees should between 75 and 150 years.

Within a plot, 10 trees with a diameter greater than 10 cm at breast height were selected for sampling. When 10 trees within a plot were not available, the number of trees required to get 10 were chosen outside the plot, but as close to the plot as possible. Two of these 10 trees which were considered to be the co-dominant trees were felled for detailed stem analysis. For each tree which under went stem analysis, the specific volume increment (SVI) was then computed. This measurement is felt to more accurately represent the growth response to environmental conditions than ring widths taken from single cores at breast height.

Increment core samples were then obtained from each of the remaining 8 trees in each plot. Each tree was cored at breast height on both the north and south side of the tree. The width of each of the rings was measured and the widths of the rings from the two cores averaged.

2.2 Climate Data

Climate data were provided to the Ontario Ministry of the Environment by the Canadian Climate Center, Atmospheric Environment Service (AES). Climate data were obtained for various weather stations in the immediate area of the established plots. These chronologies were then combined to produce a complete as possible record of the climate since 1900. The following climate variables are available as monthly means: mean temperature (°C), minimum temperature (°C), maximum temperature (°C) and total rain (mm).

3. Data Analysis

3.1 Cross Correlation

Prior to investigation of an appropriate statistical model, an attempt was made to cross correlate trees within a site and between sites within an area. Reasons for this were to identify any obvious errors made in collecting, recording or transferring the data and to investigate the utility of the climate data.

3.2 Ring Widths

Cross correlation of the tree-ring chronologies was undertaken using both $R_{i,t}$, the raw ring width at time t, for the i^th tree, data and $D_{i,t}$ where $D_{i,t} = log(R_{i,t}) - log(R_{i,t-1})$. Generally when working with time series, it is desirable to work with a de-trended series. The first difference of the log (D_t) was used to remove any long term trend. This was only possible for the data from the Kawarthas, Algonquin Park and Sault Ste. Marie areas, since the data for the other sites was provided as the means on each site. However, both the raw series and a detrended series were investigated for cross correlations.

The simple correlation coefficient was calculated as a measure of the correlation between both the raw and detrended ring widths of trees within the same plot. In general the correlation between ring widths of adjacent trees was poor. A histogram of a subsample of all the correlations based upon the raw ring widths is presented in Figure 1a. Generally the correlations on the detrended ring widths were poorer.

Two possible reasons for the poor correlations are reader error and the fact that climate may not be the limiting factor for growth. The ring structure of the Sugar Maple is referred to as diffuse-porus. The structure of the cells of the early wood and late wood each season are similar, and there is little difference in the size of the cells or the thickness of the cell walls. This makes it very difficult to measure the ring widths. Thus the structure of the tree-rings could contribute to the poor correlations.

Dendroclimatology texts indicate that trees located on "good" sites generally produce complacent rings. These are rings which do not reflect yearly variations in climate, indicating that climate may not be the main factor influencing tree growth.

3.3 SVI

Attempts to cross correlate the SVI measurements met with slightly better results. A summary of the correlations based upon the raw SVI is presented in Figure 1b.

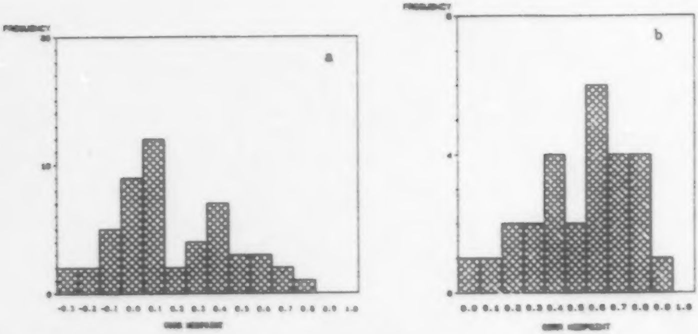

Figure 1: Histograms of the correlations between the raw ring widths (a) increments from the co-dominant trees chosen each of the plots and the raw SVI (b) increments from the co-dominant trees.

4. Proposed Tree-ring model

The model to be investigated for this study will be a general linear model treating the raw ring (raw SVI) widths as the response, and including terms for such factors as region, plot, climate, tree age, year, year by region interaction and an error. The errors associated with the rings of a tree are assumed to follow a first order autoregressive error structure. This model will regard plot as a random effect. The remaining factors and covariates will be regarded as fixed. The aggregate set of ring widths will be assumed to follow a multivariate normal distribution.

This is different from other models in the literature, since most rely on classical time series approaches, where the data is detrended prior to fitting a multiple regression model. For example, Innes and Cook (1987), Cook and Johnson (1989), and Van Deusen (1987) are examples of studies in which the ring widths are detrended using various growth curves, or low order polynomials, prior to analyzing the data. Approaching detrending in this fashion requires the assumption that the detrending curve is removing the low frequency variation associated only with the change in the growth rate of the tree related to increasing age. Zahner *et al.* (1989) uses the inverse of the age class as a regression variable to removing the low frequency variability associated with increasing age.

4.1 Autocorrelation Structure

The autocorrelation of the individual tree-ring series, will be assumed to be of first order. Thus the model becomes

$$R_t = \sum_{i=1}^{k} \beta_i x_{it} + \epsilon_t ,$$

where $\sum_{i=1}^{k} \beta_i x_{it}$ is the systematic portion of the model (to be discussed in the following section) and ϵ_t is the error term. Under the assumption of a first order autoregressive error structure,

$$\epsilon_t = \rho\epsilon_{t-1} + u_t ,$$

where u_t are assumed to be independent, normally distributed random variables with mean 0 and variance σ^2.

The method illustrated by Neter *et al.* (1983) and originally proposed by Cochrane and Orcutt (1949) will be used to estimate the first order correlation, and the estimates of the systematic component. This approach results in essentially the same analysis as suggested by Atkin (Cochrane and Orcutt 1949).

4.2 Systematic Component

4.2.1 Tree age

The volume of wood added in any given year is directly related to the age of the tree. Open canopy trees tend add decreasing amounts of wood as they age, which is characteristic of an exponential growth. Closed canopy trees on the other hand tend to follow a more complicated growth curve. This is true of the sugar maple. Thus the choice of the method for choosing a function for accounting for the geometrical constraint of adding a volume of wood to an increasing area is very important. Improperly chosen functions can either result in residuals which appear to be affected by exogenous factors or the function can remove the response of interest (Innes and Cook 1989). Both Zahner *et al.* (1989) and Innes and Cook (1989) recognize that indiscriminent detrending can obscure long term trends.

To avoid the problems induced by using a specific growth model, age related differences can removed by introducing age as a class variable in the model. The age classes are 1-5 years, 6-10 years, 11-15 years, 16-20 years, 21-30 years, 31-40 years etc. This allows the age variability to be removed, with out specifying a specific form for the growth curve. This approach has the advantage of allowing the data to specify the growth curve of the particular species, but requires that the trees collected are of a *variety* of ages, in order to separate age effects from environmental effects which vary over time.

4.2.2 Climate

A major alternative explanation of the observed reduction in growth is long term shifts in climate. Weather variables are available from the nearest weather station and will be used to adjust trends in growth due to any changes in weather patterns. Because of the multitude of potential climatic variables, variable selection techniques will be used in a preliminary analysis to select the most important.

4.2.3 Site specific factors

Permanent stand effects will be removed by including plot in the model as a random effect. This will account for permanent stand effects due to site specific characteristics such as soil, grade, and permanent climate effects.

4.2.4 Year and Region

If the above known factors do not account for all the low frequency variability, especially if there is a decreasing trend with time, there is evidence that there may be some factor as of yet unaccounted for. However, since the regions differ in many other aspects such as climate, physiography, geology and soils, it is likely that ecotypic and/or clinal ecotypic variation with respect to growth rate exists across the range of sugar maple in Ontario.

4.2.5 Year by Region interaction

The observed differences (if any) across the pollution gradient can be investigated by testing the year by region interaction. If this is significant, then there is a difference in the yearly trend between the three regions which could possibly be related to atmospheric deposition.

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A4

A Method to Establish Background Concentrations of Contaminants and Nutrients in Soil and Vegetation

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Background

The Phytotoxicology Section of the Air Resources Branch, Ontario Ministry of the Environment (MOE), in concert with the associates from the Northeast and Northwest Regions, recognized in 1971 a need to establish contaminant concentration guidelines for interpretation of environmental data. Utilizing the results of chemical analyses and available toxicological information, guidelines which were termed "Concentrations Considered Excessive" were developed for a number of contaminants in soil and plant foliage. These guidelines were utilized in Phytotoxicology investigations, with periodic revisions as deemed appropriate, notably in 1978 and 1982.

By early 1983, it had become apparent that the processes by which the Phytotoxicology guidelines had been established to date were less than satisfactory, because they varied among contaminants, were too subjective, and could not be supported by any consistent procedure or mathematical model.

After discussion among Phytotoxicology and Regional staff, it was agreed that new guidelines should be developed which would have a consistent mathematical basis and which would serve as levels which, if exceeded, would prompt further investigation on a case-by-case basis to determine the significance, if any, of the above-normal concentration(s). To this end, efforts were directed toward assembling a data base of analytical results for environmental samples collected from "background: (i.e. non-point source-contaminated) areas of Ontario".

Concurrent with these developments, a large-scale review of Ontario Regulation 308 (Air Pollution - General Regulation) was initiated by the Ministry of the Environment(1). One of the tasks of the review was the following: "Determine if Phytotoxicology standards, criteria or guidelines should be established for soil (and vegetation) deposition. Should they be incorporated in Reg. 308, or developed into a guideline?". A committee with Air Resources Branch and Regional representatives was established to examine this issue. The committee proceeded along the lines previously initiated, and developed "Upper Limit of Normal" (ULN) contaminant guidelines for terrestrial samples collected in Ontario. The concept and philosophy of the proposed Phytotoxicology ULN guidelines were then discussed at a Reg. 308 Workshop held in Toronto in November, 1985(2). The decision was made that the ULN guidelines, being statistically derived and subject to modification as new data are generated, not be incorporated in Reg. 308 but be published as a reference document(3).

As well as being a reference document in Reg. 308, the ULN guidelines, for soil, have also been incorporated in the Guidelines For The Decommissioning and Cleanup of Sites in Ontario(4) and in the proposed Dredge Material Guidelines, and the Backfill and Construction Application Guidelines.

The increased use of the ULN guidelines in other Ministry of the Environment guidelines and by other agencies and organizations and the lack of a formal review and maintenance process was brought forward by the Ontario Ministry of the Environment Materials Policy Committee(5). Accordingly, a committee, with representatives from the Phytotoxicology Section and the Northeast and Northwest Regions, was established in the spring of 1990 to completely re-evaluate the ULN guidelines.

The committee found that while the ULN guidelines were significantly better than the previous "Concentrations Considered Excessive" there still were problems with the ULN guidelines. These problems were related to the purpose for which the guidelines had originally been developed. There were problems with the land use categories, the sample categories and the model used in developing the ULN guidelines. Rather than trying to correct the problems, the committee recommended that the ULN guidelines be replaced with a new set of guidelines.

As the new guidelines were to be significantly different from the ULN guidelines a new name, "Typical Ontario Range" or "TOR", was chosen. The word "typical" does not imply acceptable the way "normal" did in the old name. "Ontario" is included in the name to indicate that the data used are only from the Ontario region. The use of "range", instead of upper limit, better reflects the new model on which the TOR's are based and how the guidelines are to be interpreted.

The TOR's are based on more and better-defined land use categories, more-specific receptor types and a model that can handle the non parametric data in the database. The new guidelines will be phased in over a two to three year period, starting in 1991, as the data become available.

Typical Ontario Range Model

There are problems with the model originally used to define the Upper Limit of Normal. The use of the mean plus three standard deviations (99.9% of the population) is not valid when the sample population is not normally distributed. As many of the data sets used were not normally distributed, the ULN guidelines determined by this method did not really represent 99.9% of the population. The second problem is the size of sample set used. Work has shown that for soils in Ontario, the number of samples needed to be within 10% of the mean 90% of the time ranges between 100 and 200 samples. Analysis of the data originally used to develop the ULN guidelines showed that using the same 10%/90% limits, the average number of samples needed would be 247. The use of 30 samples (previous minimum) could result in very poor estimates of both the mean and standard deviation for many of the ULN values.

Because of the non normally distributed nature of many of the parameters for which TOR's are to be developed and the lack of adequate statistics to handle non normal distributions properly, the use of parametric statistics in the new TOR model will be limited. The model for the new TOR will be based on the actual distribution of the data for each parameter/receptor/land use combination. The actual distribution was chosen over the range or minimum and maximum as the distribution will give the investigator more information on which to interpret results.

The data used to develop each TOR guideline will have to represent each of the MOE Regions. A minimum of 10 data points in each distribution will come from each MOE Region. In some cases, a receptor may not occur in a region, in which case, this will be noted and the TOR guideline will not apply to that Region.

In order to ensure sufficient sample size there must be enough data to be able to estimate the mean with a confidence interval of 10% and a confidence level of 90% or 50 data points, which ever is larger. The sample size is estimated using the Stein's Two-Stage Sample using the above confidence level and confidence interval. This will be the only parametric statistical test that is used in the TOR model (see (10) for a detailed description of the test). While this test is not necessarily valid for non parametric data, it is the best means of determining if there is sufficient sample to develop a TOR guideline.

Each datum point in a TOR distribution will represent a sample station. There will have to be a minimum of two samples collected from a station for that station to be included in a TOR distribution. The average of all the sample results from a station will be used. When calculating the average value for each sampling station, a result reported as <T will be used as is and a result reported as <W or < will be halved (see (8) for definition of <W and <T). A station must be in the Station Definition File (SDF) on the MOE SIS database to be included in a TOR distribution. In addition, each station must be a Control Sample Station (not influenced by a point source) for that land use category, as defined by the Phytotoxicology QA/QC Criteria Document (9).

As much of the TOR data will come from the re-analysis of archived samples, limits have to be placed on the number of samples used in order to minimize test loads. If a site was sampled in more than two years and replicate samples were collected in each year, then only one sample from each year, for a maximum of five years, will be used. If there is only one to two years of samples then duplicates for each year will be used. Where there is insufficient sample in one replicate, the replicate samples for that collection date may be combined. For archived samples, a site is defined as all samples collected within a 100 m radius.

It is the policy that as few as possible TOR's be developed by combining receptor/land use data sets in a statistically defensible manner. When it is determined that there is no significant difference between the distributions for two or more receptor types and/or land use categories for a given test parameter, the distributions will be combined into one and be identified as such. If it is determined that there are significant differences between the distributions for a receptor type for a given test parameter due to Regional differences, then a separate TOR guideline will be developed for each Region.

A set of data for a receptor/landuse category does not have to pass the 10/90 criteria of the Stein's Two-Stage Sample test in order to be tested against another set of data to determine if the distributions are different or similar. If they are similar they can be combined into one class.

The differences or similarities between distributions will be determined by using the Kolmogorov-Smirnov Two-Sample Test (see (10) for a detailed discription of the test). This is a non parametric statistical test that determines whether two distributions have the same mean, standard deviation and shape.

In addition to the TOR distribution, a value referred to as the TOR$_{98}$ will exist for each parameter/receptor/land use combination. The TOR$_{98}$ will be a value that represents the lower 97.5 percent of the sample population. The 97.5 percent was chosen as it is equivalent to the mean plus two standard deviations of a normally distributed population. The equivalent of two standard deviations was used instead of the three standard deviations used in the ULN guidelines as it was felt that it was not possible to guarantee that all of the data in a distribution are true controls. By excluding the upper 2.5 percent of the distribution, most potential outliers should be excluded. The TOR$_{98}$ value will be similar to the ULN value and can be used in a similar manner.

For interpretation purposes, all TOR's for each parameter/receptor/land use combination will be represented graphically. Each distribution will consist of a bar showing the percentile distribution, TOR$_{98}$, mean, detection limit range and a phytotoxicological threshold level (if referenced ones exist). All the land use categories for each parameter/receptor will be included in one graph. For a more detailed description of the graphical representation, see Figure 1.

Land Use Categories/Receptors/Parameters

The sections below describe ten land use categories, 18 possible receptor types and 32 test parameters that will be used in developing TOR's. The potential number of TOR's that can be developed when combined using theses categories is 5760. With ten land use categories on each graph, this will mean there will potentially be 608 pages of graphs for the fully developed TOR's. While the combining of landuse categories and receptor types when no significant differences exist will reduce the total number, the amount of work involved is considerable when compared to the ULN guidelines. Between 250,000 and 500,000 test results will be required from historical data, archived samples and newly collected samples.

Land Use Categories

The two land use categories of Rural and Urban as defined in the ULN guidelines are too broad. Land use categories that represent the different degrees of contamination due to normal human activity, past and present, are needed. The following land use categories will be assessed for TOR development:

1. URBAN
    - A. Old Urban (>40 years)
        - A1. Residential
        - A2. Parkland/Greenbelt
        - A3. Commercial/Industrial/Transportation
    - B. New Urban (<40 years)
        - B1. Residential
        - B2. Parkland/Greenbelt
        - B3. Commercial/Industrial/Transportation
2. RURAL
    1. Residential
    2. Parkland/Greenbelt/Woodlands
    3. Commercial/Industrial/Transportation
    4. Agricultural

The definition of Urban for the TOR's is not based on an arbitrary population size as it is in the ULN guidelines. Instead Urban is defined on size and density relationship. Urban is defined as any community that is fully serviced by both municipal water and sewage systems. The requirement for water and sewer services in any community is largely determined by the size of the population and the density of the housing. It is relatively easy for an investigator to determine if the services are available. Defining Urban as areas being fully serviced by municipal water and sewage services is a common practice in the Ministry of the Environment.

Urban was split into Old Urban and New Urban because many communities, such as Mississauga, Brampton and Pickering, have been built in the last 40 years, post World War II. They have not had time to accumulate the same amounts of contaminants from normal anthropogenic activities as have the old urban areas. All areas not classed as Urban are considered Rural.

Residential property includes a dwelling and associated gardens and lawns up to the dwelling side of the sidewalk or to 3 m from the road where a sidewalk does not exist.

Commercial/Industrial/Transportation includes all properties used for industrial or commercial businesses, and all designated transportation right-of-ways. For residential roadways, this would include the 3 m road allowances. Highways would include all land between the Ministry of Transportation fence lines. For railways, it would include the land between the railway fence lines or where fences are not used the area kept clear by the railway (sprayed/mowed).

Agricultural includes all land actively used as tilled cropland or pasture. Active is defined as land tilled within the last 25 years. Land not tilled within 25 years is considered Parkland. Field fence lines, although not tilled, are to be considered agricultural. Agricultural soil guidelines are to be for 0-15 cm, cultivated, depth (See Section on Soil Below).

Parkland is everything that is not residential, commercial/industrial, transportation rights-of-way, or active agricultural land. This would include parks, utility rights-of-way, golf courses, cemeteries, schools, forests or woodlots and most large undeveloped areas.

The designations for Residential, Commercial/Industrial/Transportation, and Parkland/Greenbelt are the same for all three (Old Urban, New Urban and Rural) major land use categories. Agricultural only applies to Rural. Thus, if an area is inside a municipal border but is agricultural, it is considered Rural.

Where there is no significant difference between the distribution of data for two or more land use categories for a given receptor/parameter, the categories will be combined into one.

No TOR sampling is to be conducted in areas which can not be classified. Consequently the TOR's can not be applied to samples from unclassified land use areas.

Receptor Types

Unless otherwise stated, TOR's will be developed for the major receptor groups listed below. These are essentially the same as in the ULN guidelines except that in the TOR's the groups are further broken down into sub groups, especially in the case of vegetation. This was deemed necessary as not all receptors accumulate contaminants at the same rate and they can also have different baseline levels. Where no significant differences are found between groups, the data will be combined into one TOR covering both groups.

Due to the large number of sample types and land use categories for which TOR's are to be developed, they will be created on a priority basis. The order of priority will be determined by examining the historical data to determine what sample types were collected most frequently and what land use categories were sampled most.

As the TOR's are more specific than the ULN guidelines, the TOR's can not be applied to receptors other than those for which TOR's are developed. Where TOR's do not exist for a receptor, then the old ULN guidelines may be applied. However, good control samples would be more appropriate.

Vegetation

Combining different species into one ULN and then applying that ULN to all species is not acceptable because there are distinct differences between species or families in the amount of chemical accumulation/retention that occurs. TOR's for the following most commonly collected sample types will be developed initially:

Deciduous[a] Foliage	1) maple[1] 2) birch[2] 3) aspen/poplar[3] 4) ash[4] 5) alder[5] (NE & NW only) 6) hazel[6] (NE & NW only)
Coniferous[b] Foliage	1) spruce[7] 2) pine[8] 3) cedar[9]
Grass[c]	1) green 2) mixed 3) dry
Lichens and Moss[d]	
Garden Vegetables	

[a]-Deciduous foliage includes the blade plus the petiole. All foliage in a shoot, all ages, are to be used in the sample.

[1]-maple include: Manitoba, mountain, Norway, sugar, silver, and red maples.

[2]-birch include: white and yellow birch.

[3]-aspen/poplar include: all *Populus* sp.

[4]-ash include: black, green, white and red ash.

[5]-alder include:speckled alder

[6]-hazel include:beaked hazel

[b]-The TOR guideline for coniferous foliage is to be develop for current year needles, with the exception of cedar (all non woody tissue), with the potential for expansion to older needles at a later time.

[7]-spruce include: all *Picea* sp.

[8]-pine include: all *Pinus* sp.

[9]-cedar include: white cedar

[c]-Green grass is classed as 90% or more of the sample being green. Dry grass is classed as 90% or more of the sample being dry. Mixed is all other combinations of green and dry grass. Only grasses are to be included, no sedges or rushes.

[d]-While there is a need for TOR values for lichens and mosses in the Northern Regions, further investigation as to which species should be included will have to be conducted.

Where there is no difference in the data distribution for two or more sample types for a given test parameter/land use category these will be combined into one TOR. Conversely, if there is a significant difference between one of the species in a sample category and the rest of the species in that category for a given test parameter/land use, a separate TOR will be developed for that species/parameter/land use.

The TOR's will only use data from unwashed samples and thus can only be applied to unwashed samples. For washed samples, control samples should be taken for comparitive purposes.

Tentatively, the TOR's for deciduous and coniferous foliage and grass can only be applied to foliage collected between June 15 and September 15 for the Southern Regions and June 30 and September 1 for the Northern Regions. A study will be conducted to determine what, if any, changes occur in all test parameters over the growing season in a number of deciduous and coniferous tree species. Other seasonal limits may be placed on specific species and/or test parameters if required.

A review of the 1987 SIS records showed that garden vegetables are the fifth most commonly collected receptor type for chemical analysis by the Phytotoxicology Section. TOR's will be developed for garden vegetables after a thorough analysis of the SIS records from 1981 to 1990 to determine which of the many garden vegetables require TOR's. TOR's for garden vegetables will be limited to the three residential land use categories and possibly the Urban Parkland category.

Soil

TOR's for soil will only apply to the 0-5 cm depth, except for tilled areas (gardens and fields), 0-15 cm depth. Guidelines for the following three soil classes will be developed.

Soils Class 1) Organic carbon content <17%, sand >70% and clay >15% by weight
(all soils not in class 2 or class 3)
2) Organic carbon content >17% by weight
3) Sand content >70% and clay <15% by weight
(sandy loam and sand soils as defined in (11))

Clay and sand content is determined in the field by each investigator using the standard "Finger Assessment of Soil Texture" method (11). Organic content as determined by loss on ignition.

Due to the different ability of these soil classes to retain contaminants, there is a potential for significant differences between these three soil types. Further study will determine the actual significance. Initially, all existing soil data and archived samples, 0-5 cm, will be used and considered as being in Soil Class 1.

Snow

TOR's for snow samples will be developed for the Northeast and Northwest Regions only. These will be for snow samples collected using the standard Phytotoxicology technique (6) in which the entire snow profile is collected. The TOR will be expressed on an area loading basis (mg/m2/day) and not on the weight per volume basis (mg/l) used in the ULN guidelines.

Moss Bags

There are potential problems with developing TOR's for moss bags. The major problem is that the background level of a number of elements can vary significantly with the source of the moss. Thus, each new batch of moss may have a different starting level. As the exposed control moss bag accumulation is small, significant differences between batches can greatly affect the TOR guideline. There also may be problems in the interpretation of any data from moss bags that come from batches not included in the TOR. The other problem is that, for some elements, the level in exposed control bags is often lower than unexposed bags.

Because of the above problems, plus the fact that moss bags are really an artifical tool and not a naturally occuring receptor it has been decided that TOR's will not be developed for moss bags. As it states in this document that ULNs will be used were TOR's do not exist, and as there are ULNs for moss bags, the ULNs for moss bags will be rescinded as of the publication of the Version 1.0 of the TOR document.

Analytical Parameters

The analytical parameters for which TOR's will be developed (vegetation, soil, moss bags and snow) are given in Table 1. TOR's may be developed for tritium and radium for certain sample types if the data become available from a Federal/Provincal cooperative study.

TOR's will not be developed for organic compounds at this time. The reliability of the old data is questionable. The number of samples per receptor needed is unknown. The number of potential compounds is large. The cost, especially for PAHs and dioxins, of developing TOR's for organics would be large. A demonstrated need for a TOR guideline will be required on a compound by compound basis before the necessary work and resources will be committed to developing a TOR guideline for any organic compounds.

For reference purposes, the instrumentation, sample digestion and/or preparation and the minimum sample weight currently used by the Laboratory Services Branch, Inorganic Trace Contaminants Section, for each test will also be given. All samples collected for TOR's should have four times the minimum weight required for analysis. This will allow enough sample for re-analysis by the lab and for archiving of the sample for future analysis.

The inorganic analytical parameters for which TOR's will initially be developed, for the three major receptor types Vegetation, Soil and Snow, are listed in Table 1 below.

Table 1: Analytical Parameters for Which TOR's Will be Developed for Vegetation, Soil and Snow

Test Parameter	Vegetation Foliage & Grass	Soils 0-5 cm	Snow
Aluminum	X	X	X
Antimony	X	X	X
Arsenic	X	X	X
Barium	X	X	X
Beryllium	X	X	X
Boron	X	X	
Cadmium	X	X	X
Calcium	X	X	X
Chloride	X	X	X
Chromium	X	X	X
Cobalt	X	X	X
Copper	X	X	X
Fluoride	X	X	X
Iron	X	X	X
Lead	X	X	X
Magnesium	X	X	X
Manganese	X	X	X
Mercury	X	X	X
Molybdenum	X	X	X
Nickel	X	X	X
Total Nitrogen	X	X	X[a]
Total Phosphorus	X	X	X
Total Potassium	X	X	X
Selenium	X	X	X
Silver	X	X	
Sodium	X	X	X
Strontium	X	X	
Sulphur	X	X	X[b]
Titanium	X	X	X
Uranium	X	X	X
Vanadium	X	X	X
Zinc	X	X	X
Conductivity			X
Sus. Solids			X
Dis. Solids			X
Tot. Solids			X
Dis. Org. Carbon			X
Dis. Inorg. Carbon			X
Part. Tot. Carbon			X

a - nitrogen as nitrate, b - sulphur as sulphate

Review and Maintenance Process

Because of the scope of the TOR's, it will take a number of years to develop TOR's for all of the receptor type/land use combinations. In addition, new sample types and parameters will be added as the need arises. The TOR's will be a continually evolving set of guidelines. This will require the TOR committee be a regularly sitting body that will provide the basis for regular review and maintenance of the TOR's.

The committee will consist of one representative from the NE and NW Regions and six representatives from the Phytotoxicology Section. A minimum of half of the members should be regular field investigators to ensure that their requirements are being met.

The TOR committee will hold a series of meetings starting in the beginning of each calendar year to evaluate the data collected in the previous year for inclusion into the TOR's. The committee will also develop a work plan for the gathering of additional data for the next field season. The committee will coordinate its efforts with the Ontario Ministry of the Environment Materials Policy Committee and other relevant committees.

In order to handle the regular updating of the TOR's, the Phytotoxicology Integrated Information Management System (PIIMS) will be modified. PIIMS will identify all new data that fit the TOR criteria and will automatically update the TOR tables and graphs at the end of each year. The TOR committee will be responsible for validating these changes.

Interpretation and Application of the Typical Ontario Range

The Ministry of the Environment "Typical Ontario Range" (TOR's) for soil, vegetation, moss bags and snow were developed by the Phytotoxicology Section of the Air Resources Branch, in concert with associates from the Northeast and Northwest Regions, to assist in the interpretation of Phytotoxicology data. The TOR's are to assist in determining whether the level of a measured parameter in a given receptor is significantly above that which would be anticipated for the level of anthropogenic activity in the area sampled (land use category). An exceedance of the TOR would indicate a potential point source of contamination.

As the TOR's are also a set of distributions, they can also be used to determine where, in the anticipated distribution, a result falls. This can be used to indicate a potential level for concern even when a result falls within the range.

These guidelines apply only to samples collected using standard Phytotoxicology sampling techniques(6), prepared using standard Phytotoxicology laboratory sample preparation techniques(7) and analysed using standard MOE analytical techniques (8). As the TOR's are developed from data collected in Ontario, or specific regions of Ontario, they only apply to terrestrial samples collected in Ontario or a specific region of Ontario.

The TOR's should not be the sole means by which results are interpreted. In interpreting results importance should be placed on the control samples that are collected and on the pattern of contamination observed in the samples. The TOR's are to assist where there is some question concerning the local background samples and/or enough samples have not been collected to determine any pattern of contamination (i.e. complaint investigations). The TOR's for each receptor/land use category assume a given range of contamination resulting from normal anthropogenic activity for that land use category. As a result, the TOR's should not necessarily be considered as acceptable levels nor do they imply phytotoxicity. The one potential exception to this rule is for the Rural Parkland/Forest land use category where it can be assumed that there has been minimal impact, except for long range transport, from anthropogenic sources.

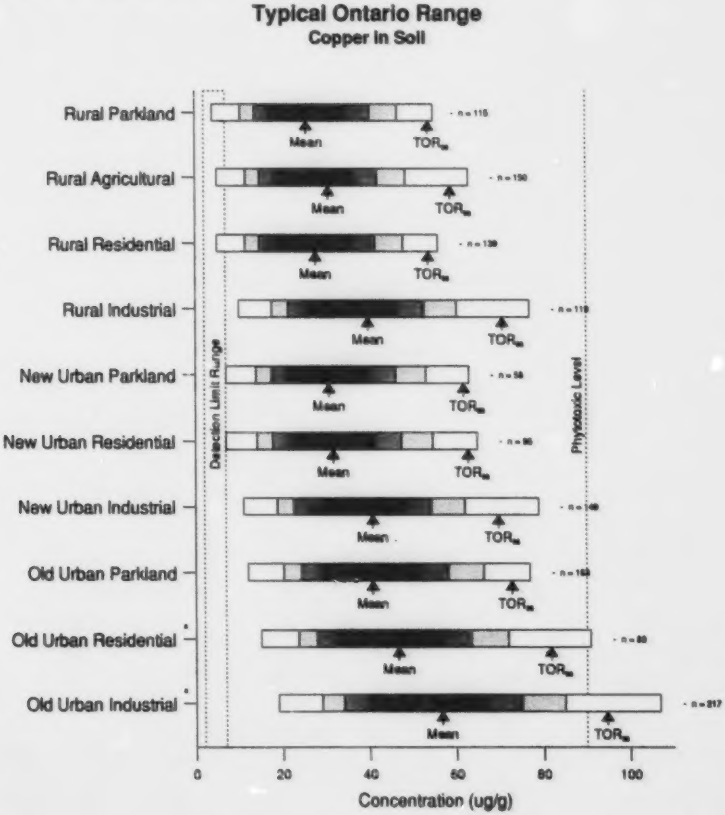
Where a TOR exists for a given receptor/land use category, the TOR will supersede the ULN for the interpretation of results. If a TOR does not exist, the ULN will be used.

The use of the TOR for purposes (i.e. incorporation into other Ministry guidelines or standards) other than those described above should be done with caution and with prior consultation with the Phytotoxicology Section.

Typical Ontario Range Distributions

No TOR's exist at this time. An example of what a typical TOR graphic will look like is given in Figure 1 below. It is anticipated that TOR's for soil and maple vegetation for the Rural Parkland land use catagory will be developed by the spring of 1991. As TOR's are developed, they will supersede the ULN guidelines for the interpretation of data. In all other cases, the ULN guidelines will be used for the interpretation of data.

Figure 1: Hypothetical Example of a TOR for Copper in Soil



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FURTHER DEVELOPMENTS IN THE ANALYSIS OF THREE DIMENSIONAL ENVIRONMENTAL DATA

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Air quality data is commonly analyzed by a variety of methods that treat the data characterizing the atmosphere at a site over time, or for a single chemical constituent over space, or over time. All of these two dimensional analyses fail to provide the full information content of the data to the investigator since the atmosphere is really represented by three dimensional data; compositional data taken at multiple sites (space) and times. To analyze such data, three dimensional statistical methods are needed. We have previously reported on our development of three-mode factor analysis. In order to provide more quantitative interpretation of data sets, we have explored the development of target transformation three-mode factor analysis. In simulated data sets representing the composition of airborne particulate matter, we have attempted to recover the original source profiles and source contributions to the aerosol mass. However, we have found that we could not adequately reproduce the data even in the absence of error. If error-free data cannot be adequately reproduced, this model cannot be applied to real world data. Thus, an alternative approach, direct trilinear decomposition, has been explored. This method also decomposes the three dimensional data matrix in a series of matrices that can be interpreted in terms of source compositions and contributions. With simulated data with and without data, excellent reproduction of the correct results were obtained. The mathematical basis of these methods along with the results of these exploratory studies will be presented.

Introduction

Dispersion modeling and receptor modeling are two types of techniques used in air quality management. Dispersion models have been used in this field for a long time. For dispersion modeling, a major effort is usually needed including a survey of emissions over the studied area, collection of meteorological data, field tests to determine the dispersion parameters, mechanistic studies on the chemical transformation and scavenging between phases, as well as the studies of the models themselves. There are a number of difficulties associated with these steps in dispersion modeling (Budiansky, 1980; Gorden, 1980, 1988). Budiansky (1980) has discussed the problems of dispersion models, for example, the error in emission inventories, the uncertainty in the horizontal and vertical dispersion parameters, low availability of complete information and high cost for complex models, etc. In addition, dispersion models can only handle the sources that are known to contribute to the system. It cannot include the sources that are unknown or where lack of emission data makes a source unmodelable.

In last two decades, receptor modeling has played a larger and larger role in air quality management. Receptor models in contrast to dispersion models utilize the data collected at receptor sites to elucidate information on properties and influence of emission sources. In typical receptor models, ambient samples are analyzed yielding their chemical compositions. These data can then be analyzed so that the sources can be identified and their contributions to the collected sample mass can be estimated. This procedure is also called source apportionment. The estimates of the source contributions for an airshed are useful information in developing air pollution control strategies.

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A variety of receptor models have been developed. There have been several major review articles (Gorden, 1980, 1988; Cooper and Watson, 1980), a number of symposium books (Macias and Hopke, 1981; Dattner and Hopke, 1983; Pace, 1986; Watson, 1989), and one comprehensive book (Hopke, 1985) reviewing and describing the principles and applications of these models. The ultimate purpose of receptor modeling is to qualitatively identify the pollution sources at the receptor sites and quantitatively estimate their mass contributions. A three-way table of air quality monitoring data provides information on the spatial and temporal variations of the pollutants. A model based on such a data set potentially has more power to identify the sources and estimate the contributions than the traditional methods do.

Three-Way Data Analysis

Air pollution systems are typically characterized by taking samples over time at a number of sampling sites. These samples are then characterized by a variety of analytical methods so that the data set can be represented by a data block as illustrated in Figure 1. The term "three-way data table", or "three-way matrix", or "three-mode matrix" are used to describe this kind of data

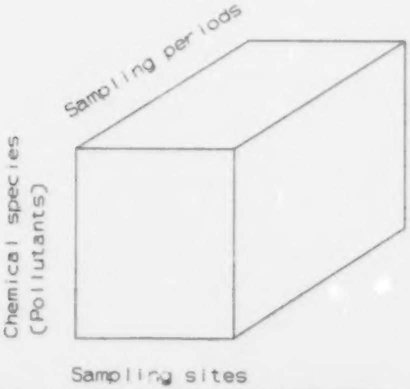

Figure 1 Typical structure of the data gathered for air quality management.

sets. Such a data set provides information on the simultaneous temporal and spatial variations in the system. However, conventional (two-mode) principal components analysis methods are really designed to analyze a data rectangle obtained by taking a slice of the block in one of the three orthogonal directions. For factor and principal components analysis, this slice is typically the measured concentrations at a single location over time. The empirical orthogonal function (EOF) approach analyzes a single species concentration over sites and time (Peterson, 1970). One can also perform a spatial analysis of elemental concentrations over sites for a single time interval. However, each of these methods is only looking at a single plane in the data block.

Another factor analysis method called three-mode factor analysis (TMFA) has been developed by Tucker (1966) and Kroonenberg (1983). This method works directly on the full three-way data matrix as its input, and thus can examine variations among all three modes simultaneously. The ability to examine three-way observational data suggests the potential utility of TMFA in receptor modeling. TMFA (Zeng and Hopke, 1990) provides a technique to analyze such a complicated system and condense the system variations in a smaller core matrix as a summary of the system. Unfortunately, TMFA could not provide the mass contributions. A modified version of Target Transformation Factor Analysis, TTFA, (Hopke, 1988) was explored by Zeng (1990). However, this approach could only achieve a semi-quantitative analysis because it does not take full advantage of three-dimensional variations. A new model called direct trilinear decomposition (DTD) can potentially overcome the problems identified with the other three-mode approaches as well as the two-mode models.

The development of a DTD model in receptor modeling has evolved from the work by Sanchez and Kowalski (1990). They developed the DTD method to process the data obtained in analytical chemistry with instruments that generate two-dimensional arrays of data for multiple samples. Their example was a three-way data set of emission-excitation fluorescence spectra for three mixtures of three organic compounds. With their DTD method, the emission and excitation spectra of all three compounds were predicted and the relative concentration of the compounds in the mixtures were calculated.

The DTD method appears to be a quantitative method for three-way data. In order to apply DTD in receptor modeling, a major difficulty had to be overcome. This problem was how to relate pollution sources to the model. In the example of Sanchez and Kowalski (1990), each organic compound had two spectra, an emission spectrum and an excitation spectrum. In fact, DTD model is applicable for a multiple sample system with two-dimensional spectral surfaces. A source profile in a receptor modeling problem can be considered to be one spectrum. Then another spectrum-like property of the pollution source is needed. This problem and others concerning the application of DTD in receptor modeling were resolved by methodological studies using simulated data sets. The results of these studies are presented in this report.

Theory of Direct Trilinear Decomposition

The trilinear model will be introduced by comparing linear and bilinear models in mathematical sense. The comparison of DTD will also be made with the general mass balance receptor models. The atmospheric mass balance problem can be expressed as a linear model.

$$x_{ijk} = \sum_{n=1}^{N} y_{in} z_{njk} + \epsilon_{ijk} \tag{1}$$

where x_{ijk} is ambient concentration of species i at sampling site j in period k, [ng/m^3], y_{in} is the concentration of i in the particles coming from source n, [ng/μg], z_{njk} is the mass contribution of source n at site j in period k, [μg/m^3], N is number of source types and ϵ_{ijk} is the error. This expression describes the typical multivariate linear model.

If z_n is expanded to a vector, the model become a bilinear model:

$$\boldsymbol{X} = \boldsymbol{YZ}+\boldsymbol{E} = \sum_{n=1}^{N} \boldsymbol{y}_n \otimes \boldsymbol{z}_n + \boldsymbol{E} \tag{2}$$

where $\boldsymbol{X}$ is a $I \times J$ two-way matrix, and $\boldsymbol{Y}$ and $\boldsymbol{Z}$ are $I \times N$ and $N \times J$ matrices, respectively. Their n-th column vectors are $\{\boldsymbol{y}_n\}$ and $\{\boldsymbol{z}_n\}$. The sign $\otimes$ represents an outer product. A term $\boldsymbol{y}_n \otimes \boldsymbol{z}_n$ (called a dyad) is equivalent to the matrix product $\boldsymbol{y}_n \boldsymbol{z}_n^T$. $\boldsymbol{E}$ is the error matrix equivalent to ϵ in the linear model [equation 1]. Considering $\boldsymbol{E}$ to be the model residual term, TTFA is actually a bilinear model.

The bilinear model can be expanded to a trilinear model by adding another term in third mode. If $\boldsymbol{a}_n$, $\boldsymbol{b}_n$, and $\boldsymbol{c}_n$ are used for the vectors in three modes, the trilinear model can be expressed as:

$$\boldsymbol{X}_{ijk} = \sum_{n=1}^{N} \boldsymbol{a}_n \otimes \boldsymbol{b}_n \otimes \boldsymbol{c}_n + \boldsymbol{E}_{ijk} \tag{3}$$

Note that $\boldsymbol{X}_{ijk}$ and $\boldsymbol{E}_{ijk}$ represent three-way matrices, and x_{ijk} and e_{ijk} are their corresponding elements. The number of elements in the vectors $\boldsymbol{a}_n$, $\boldsymbol{b}_n$, and $\boldsymbol{c}_n$ are I, J, and K, respectively.

In Sanchez and Kowalski (1990), $\boldsymbol{X}_{ijk}$ was a three-way data table with the i mode for emission wavelength, the j mode for excitation wavelength, and the k mode for sample. With DTD, the data set was decomposed into $\boldsymbol{a}_n$ standing for emission spectrum of compound n, $\boldsymbol{b}_n$ for excitation spectrum of compound n, and $\boldsymbol{c}_n$ for relative concentration of compound n in the samples. The compounds were identified by their spectra ($\boldsymbol{a}_n$ and $\boldsymbol{b}_n$), and their relative concentrations were obtained in $\boldsymbol{c}_n$.

The trilinear model may be considered to be a special case of TMFA model (Zeng and Hopke, 1990). Equation 3 can be rewritten in scaler form.

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk} \tag{4}$$

The trilinear model is also called Parallel Factor Analysis (PARAFAC) or CANDECOMP model in the psychology literature (Kroonenberg, 1983; Harshman, 1970, 1976; Carroll and Cheng, 1970). The procedure for performing a trilinear decomposition based on the model in equation 3 is given by Zeng (1990) and is based on the work of Sanchez and Kowalski (1990).

DTD Applied in Receptor Modeling

The key to applying DTD in receptor modeling is to establish the relationship between the terms in the model [equation 3] and the physical properties of the airshed. If the three-way data matrix is arranged such that mode 1 (*i*) corresponds to the chemical species, mode 2 (*j*) to sampling time, and mode 3 (*k*) to site, the *N* vectors $\{a_n\}$ can represent the source profiles. Two new concepts are introduced so that the model can be fitted into the physical system. "Emission pattern" is used to reflect the relative variations of source emission strength changing with time at the receptors. Like a source profile, the emission pattern can be considered to be another property of a source. Each source has its own emission pattern. With the source profile and emission pattern, a source can be characterized more completely and accurately. The vectors $\{b_n\}$ in the model then correspond to the emission pattern.

Another concept, the site coefficient, is introduced to refer to the vectors $\{c_n\}$ in equation 3. The site coefficients indicate the variation in source strength from site to site. With these definitions, a three-way air quality data set could be decomposed into source profiles (a_n), emission patterns (b_n), and site coefficients (c_n). The mass contribution of source *n* at site *k* in time *j*, $\bar{z}_{njk}$, can be obtained by combining the emission pattern and the site coefficient.

$$\bar{z}_{njk} = b_{jn} c_{kn} \tag{5}$$

If the source profile $\bar{y}_{in}$ is defined as

$$\bar{y}_{in} = a_{in} \tag{6}$$

the model in scaler form becomes:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} = \sum_{n=1}^{N} \bar{y}_{in} \bar{z}_{njk} \tag{7}$$

The scale of $\bar{y}_{in}$ and $\bar{z}_{njk}$ do not necessarily agree with the actual scale of source profiles and contributions. Similar to TTFA, a regression procedure can be used to find a set of scaling coefficients, $s = \{s_n\}$, such that

$$x_{ijk} = \sum_{n=1}^{N} \left[\frac{\bar{y}_{in}}{s_n}\right] (s_n \bar{z}_{njk}) = \sum_{n=1}^{N} y_{in} z_{njk} \tag{8}$$

where y_{in} and z_{njk} are the scaled source profiles and contributions. The regression is based on

$$mass_{jk} = \sum_{n=1}^{N} z_{njk} = \sum_{n=1}^{N} s_n \bar{z}_{njk} \tag{9}$$

Studies with Simulated Data Sets

The DTD method was tested with simulated data sets. A simulated data set was created using the same three source profiles as used in the second simulated data set presented by Zeng and Hopke (1990). Twenty species were considered. It was assumed that the emission pattern of source 1 is a random pattern, and the pattern of sources 2 and 3 are periodic with different periodicities. Figure 2 shows these patterns, along with the formulae used to generate them. Mode 2 contains 18 sampling periods. Assume there are 4 sites with site coefficients assigned in Table 1. The simulated data set was produced using equation 1. The contributions, z_{njk}, in equation 1 were obtained from the emission patterns and site coefficients.

The DTD method was applied to the simulated data set without added errors. The results were perfect. Both the source profiles and source contributions estimated by the model were exactly same as the true values. Several other simulated data sets with different source profiles were tested and the model gave the same excellent results. These tests show the general validity of proposed method.

Tests need to be made to investigate the sensitivity of the model to the possible error components existing in the system. The primary error components in the system include measurement errors in the ambient concentrations (i.e. errors in X_{ijk}), and possible fluctuations in the source profile concentrations (y_n). Collinearity is another important factor that may cause large errors in the model output. Collinearity problems occur when two or more sources have similar source profiles. The correlation coefficient between two source profiles can be used to measure their similarity.

In order to investigate the influence of these factors, two more simulated data sets were created in addition to data set I. The only difference between data sets II and III and data set I is the source profiles. Source profile 2 in these data sets was created in such a way that the

Table 1 Site coefficients for the data set IV

Site	Source 1	Source 2	Source 3
1	50	50	50
2	50	50	100
3	100	50	100
4	150	150	200

correlation coefficients between source 1 and source 2 increase from 0.525 in data set I to 0.836 in data set II, then to 0.977 in data set III. These source profiles are listed in Table 2.

Errors were added to the simulated data sets. Two types of errors were considered. One was the errors associated with ambient sampling and analysis. The other was fluctuations of the

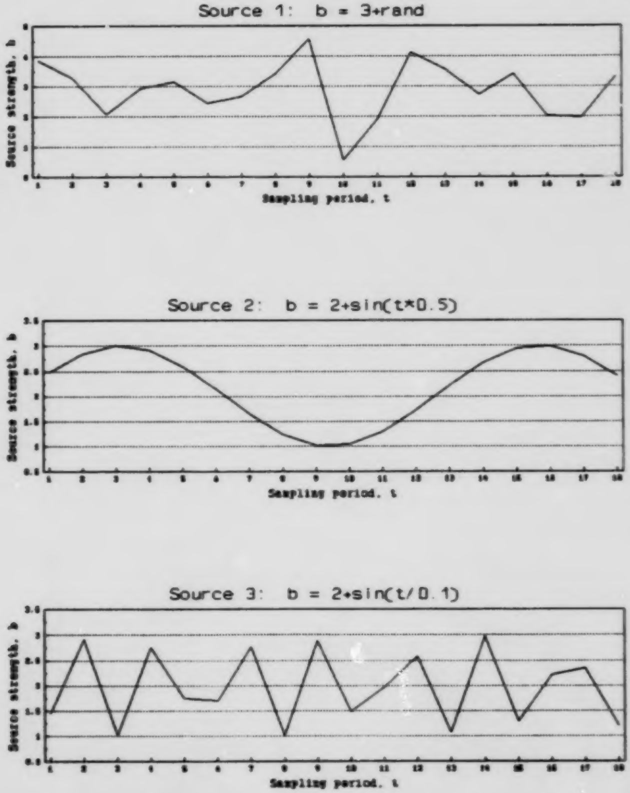

Figure 2. The source emission patterns used in the simulated data sets.

Table 2 Source profiles used in the data sets I, II, and III

No.	Element	Source 1	Source 2 in set I	Source 2 in set II	Source 2 in set III	Source 3:
1	Na	9.7	5.9	5.9	5.9	1.4
2	Al	26.	8.8	17.6	13.2	2.5
3	Si	150.	47.	105.5	61.3	5.
4	S	15.	71.	71.	18.8	40.
5	Cl	11.	12.	12.	8.8	11.
6	K	10.	6.3	6.3	6.7	5.
7	Ca	23.	11.5	11.5	14.5	5.
8	Ti	2.6	1.7	1.7	1.7	2.8
9	V	0.48	1.7	1.7	0.7	0.01
10	Cr	0.4	0.9	0.9	0.4	1.
11	Mn	0.48	6.5	6.5	0.5	0.22
12	Fe	18.	10.7	10.7	10.7	44.
13	Ni	0.2	0.7	0.7	0.7	250.
14	Cu	1.3	3.2	3.2	0.7	2.
15	Zn	3.2	32.	32.	1.9	1.9
16	As	0.3	3.	3.	0.3	0.05
17	Se	0.11	1.1	1.1	0.05	0.05
18	Br	0.2	1.3	1.3	0.05	0.84
19	Sb	0.03	0.9	0.9	0.05	0.05
20	Pb	2.	8.2	8.2	1.2	10.

source profiles. The notations e_x and e_y are used for the former and latter errors, respectively. The errors were added by the following equation:

$$x_{ijk} = \sum_{m=1}^{N} (y_{im} + e_y^{(ijk)})\, z_{mjk} + e_x^{(ijk)} \tag{10}$$

The errors $e_y^{(ijk)}$ and $e_x^{(ijk)}$ were normally distributed random numbers. A random number generator was invoked for every i-j-k combination. The magnitude of the errors is controlled by a parameter *h*:

$$\begin{aligned} e_y^{(ijk)} &= h_y\, y_{im}(rand) \\ e_x^{(ijk)} &= h_x\, x_{ijk}(rand) \end{aligned} \tag{11}$$

where *rand* is a random number generator producing normally distributed random numbers with a mean of 0 and a standard deviation of 1, e.i. *N(0,1)*. Source profile variations are more likely to

Table 3. Descriptions of the simulated data sets used for DTD tests

Simulated data set	Highest correlation coefficient between source profiles	error level in ambient measurement, h_x (%)	error level in source profiles, h_y (%)
I	0.525	0	0
I(A)	0.525	1	0
I(B)	0.525	1	1
I(C)	0.525	4	0
II	0.836	0	0
II(A)	0.836	1	0
II(B)	0.836	1	1
II(C)	0.836	4	0
III	0.977	0	0
III(A)	0.977	1	0
III(B)	0.977	1	1
III(C)	0.977	4	0

be log-normal than normal (Currie *et al.*, 1984), but normally distributed errors were used in these preliminary tests. If h_y is chosen to be 0.01, there will be roughly 1% fluctuations around the true y_{ik} values. These modifications to the data sets were designed to simulate the real situation in the atmosphere. The source profiles may fluctuate around the mean values from time to time and site to site. After the particles are collected in a sample with a certain mass and an actual chemical composition, there will be errors in measuring that composition. This simulation method was used in all three data sets with different error levels. The data sets generated from same base (same true source profiles and contributions) are designated with letter "(A)", "(B)", "(C)", ... following the notation of the base set (Table 3). For example, data set I is a base set (error-free). Data set I(A) is from the same base with 1% level of errors added in X_{jk} matrix.

The DTD method was applied to these simulated data sets. The results are summarized in Table 4. The correlation coefficients between true and estimated source profiles indicate how close the estimated profile are to the true profiles. The APPRAE [see Zeng and Hopke, 1990] is used to measure the goodness of model estimation of source contributions. As mentioned before, the DTD method always gives the true solutions for error-free data sets. When errors exist in the data sets, the method identified the sources very well and the estimated source contributions were reasonably good. The APPRAE values increase as error is added at higher and higher levels. For same error level, the error in the model estimation increase as the collinearity increases (from data set I to III). Note that when the two sources are highly collinear (correlation coefficient of

Table 4 Results of DTD and TTFA for the simulated data sets

Simulated data set	Source profiles: the correlation coefficients						Source contributions: APPRAE (%)	
	DTD			TTFA			DTD	TTFA
	S1	S2	S3	S1	S2	S3		
I	1	1	1	1.00	0.98	1.00	0	9.56
I(A)	1.00	1.00	1.00				2.77	
I(B)	1.00	0.99	1.00	1.00	0.95	1.00	5.35	14.95
I(C)	0.98	0.89	1.00				10.89	
II	1	1	1				0	
II(A)	1.00	1.00	1.00				11.30	
II(B)	1.00	1.00	1.00	1.00	0.99	1.00	10.34	14.48
II(C)	0.94	0.97	1.00				71.41	
III	1	1	1				0	
III(A)	1.00	0.97	1.00				13.46	
III(B)	1.00	0.98	1.00				13.06	NS[a]
III(C)	0.99	0.98	1.00				58.37	

a: NS = No solution (source not identified or large negative mass estimated).

0.977), the model still can identify the sources and estimate the contributions in a reasonable range. In analyses of data sets III(A) and III(B), it is nearly impossible to identify sources 1 and 2 by looking at the estimated source profiles (y_n or a_n). However, the two sources can be distinguished by examining their emission patterns (b_n). This result shows a unique feature of DTD model.

Several data sets were also analyzed by TTFA to compare the TTFA and DTD models. The TTFA was performed individually on each slice of the data set. The analysis was in Q-mode. Since the iterative target transformation did not produce source profiles as well as DTD did, there were larger errors in estimated contributions. When two sources were highly collinear, TTFA failed. TTFA identified only two sources. If three sources were retained, the contributions of one source were large negative values. All of the comparisons in Table 4 show that DTD performed better than TTFA.

Another advantage of DTD method is that there are no trial and error procedures involved. In TTFA, the modeler needs to decide which target vector or vectors produced by the iteration from unique vectors should be selected. The results will depend on these selections. The combination of these vectors for final results is also trial and error based method. It is usually time consuming. The DTD procedure is straight forward, and it is more objective. The

DTD is more efficient because it analyze the whole three-way data set at once.

The DTD model does not require prior knowledge of the sources. An alternative approach to solving equation 1 is to use a regression analysis with known source compositions. This approach is called a Chemical Mass Balance (CMB) analysis. However, the modeler needs to know what kind of sources exist in the system, and what their source profiles are. The results rely heavily on the quality or the source profiles inputed into the model. However, it is often difficult to find suitable and accurate source profiles. In practice, collinearity is also a problem with CMB (Cheng *et al.*, 1988). DTD is potentially a useful method to overcome the collinearity problem because of the additional dimensions that can be examined.

In all receptor models, it is assumed that the chemical compositions of the sources (source profiles) are constant from sample to sample. In a real atmospheric system, the source profiles will fluctuate around their means. The bigger the fluctuations, the larger the errors will be in the model estimations. The DTD model requires the same assumption. In addition, the DTD model also requires that the source emission patterns are same for all sites. For instance, if the source strength goes down by 30% from sampling period 1 to period 2 at one site, the same percentage decrease should be observed at other sites although each site may have its own absolute value. This assumption implies that local influences on the sites should be minimized when designing the sampling network.

Conclusions

A basic methodological study of direct trilinear decomposition as a receptor model has been conducted. The DTD model results showed some very attractive features, including the capability to distinguish similar sources, better accuracy and simpler procedures compared with TTFA. More methodological studies are needed, for example, a study of the determination of the number of sources (N). The number of sources could be determined based on the eigenvalues or based on some type of residuals analysis. Sanchez and Kowalski (1990) suggested "that a slight overdetermination of N does not affect the resolved spectra as much as underestimation", but they did not give a better way to resolve this "elusive" question. Applications to real data sets will then be needed to see how effective the approach can be in resolving the full complexity of the receptor modeling problem.

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EVALUATING THE COMPREHENSIVE MODEL ADOM

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1. Introduction and Brief Model Description

The Acidic Deposition and Oxidant Model (ADOM) was developed to study the response of acidic deposition to various emission scenarios. Before the model can be applied with confidence, its simulation of the current verifiable scenarios must be evaluated. This paper briefly describes three such tests. The details of ADOM development are given in ERT (1984).

ADOM is a three-dimensional Eulerian model with 12 vertical layers extending from ground up to 10 km and for a horizontal grid spacing of 127 km by 127 km over the 33 x 33 grid domain depicted in Figure 1.

The modules in ADOM are:

Transport: advection and diffusion in 3-D based on a cell-centred flux formulation.

Gas-phase Chemistry: 47 species involved in 114 species representing the major sulphur, nitrogen and oxidant reactions.

Cloud Physics: cloud transport and mixing simulated by a stratiform and a cumulus module with parameterized cloud microphysics.

Aqueous-phase Chemistry: 13 air and aqueous species involved in 25 chemical and transfer reactions.

Dry deposition: deposition velocity modelled as the inverse sum of the aerodynamic, deposition layer and surface canopy resistances.

The input to drive ADOM are:

Emissions: SO_2, SO_4^{2-}, NO_x, NH_3 and 10 categories of reactive hydrocarbons in 3-D and with appropriate temporal variations.

Meteorology: wind, temperature, relative humidity, eddy diffusivity and cloud information, for transport, cloud and chemical processes, given in 3-D. The Canadian Meteorological Centre's spectral weather prediction model is used as a dynamic interpolator between observations. A 1-D boundary layer model enhances the resolution of these data close to the ground.

Geophysical: Land use and terrain data for dry deposition and micrometeorological calculations.

2. Model Performance Evaluations

Simulations of a spring, a winter and a summer period are presented. The first few days of each simulation are used to "start up" the model and the evaluation of the model's performance was made on the remaining days. Since the first two simulation periods have limited observational data, this paper will emphasize on the evaluations with the EMEFS data.

2.1 The Spring Simulation

ADOM was run for the period from April 10 to April 29, 1981 during the OSCAR (Oxidant Scavenging and Characteristics of April Rain) field experiment. A series of frontal disturbances tracked through the northern United States and southern Canada over the 20-day period. Shower activity dominated in the western half of the domain with a mixture of drizzle, rain and showers in the east.

Observed daily average SO_4^{2-} concentrations in precipitation were available at 34 sites in the northeastern U.S. and southern Ontario for 5 days during this period. A scatter graph of modelled versus observed SO_4^{2-} concentrations in precipitation averaged over OSCAR II (April 13-14) and OSCAR IV (April 22-24) is given in Figure 2. The average model results showed little bias and more than 70 and 80% of the modelled results were within a factor of 2 of the observations. Given possible errors in the input NH_3 and NO_x emission data as well as the fact that a modelled grid average is being compared to point measurement, these results are encouraging.

2.2 The Winter Simulation

ADOM was run for the period from January 28 to February 7, 1985 with the first day used as a startup. Model predicted SO_4^{2-} concentrations in precipitation were compared with observations from the Acid Deposition System (Figure 3). The large scatter in this graph can partly be explained by the large scatter found between model grid average precipitation and that observed at the measurement sites. Figure 3 shows that results with only a single day of precipitation over the 10-day period were worse than multi-day averages (i.e. precipitation is more consistent across a grid for a multi-day average). The nitrate/sulphate ratios in precipitation were higher during this winter episode than in the spring simulation (1.6 in winter and 0.8 in spring). This compares with the observed ratios (2.4 in winter and 0.9 in spring).

For other species observed data were very limited but the model overpredicted SO_2 air concentrations and systematically underpredicted air concentrations of sulphate and nitrate.

2.3 The Summer/Fall Simulation (EMEFS)

The Eulerian Model Evaluation Field Study was conducted over eastern North America from July 15 - October 6, 1988 to gather data in three dimensions to evaluate comprehensive models of long-range transport (Barchet and Dennis, 1989). A 12-day period from July 28 - August 8 and a 37-day period from August 25 - September 29, 1988 were simulated. Preliminary comparison of the two periods shows similar characteristics. The results of the latter period are discussed in detail below.

The monitoring sites of EMEFS are grouped into regions (see Figure 1) according to meteorological and emissions characteristics so as to provide greater clarity to the analyses. In the scatter plots presented below, the symbols refer to the regions. Each point in the scatter plot is a weighted average over the available daily observed and predicted data between August 27 - September 29, 1988.

Figure 4 presents the comparison of the modelled and observed **ground level SO_2 in air**. All but five points are overpredicted. Out of the heavy emissions area represented by Regions 2, 5 and 6, only one station shows an underprediction. The stations for light emissions area represented by Regions 1, 3, 7, 8 and 9 are mainly found in the lower half of the observed and predicted ranges.

Figure 5 presents the comparison of the modelled and observed **ground level SO_4^{2-} in air**. All except 3 points are underpredicted. The 3 points that are not underpredicted are in remote regions either upwind or downwind of heavy source areas. The values of these remote regions (1 and 3) are confined to the lower half of the predicted and observed range of values. The higher values in the plot have in general a larger absolute underprediction. The largest predicted value is 6.7 $\mu g\ m^{-3}$ while the largest observed value (not the same point) is over 10 $\mu g\ m^{-3}$. It seems like the predictions have reached a limit and cannot increase further. Analysis of the early period (July 28 - August 8, 88) shows an even more drastic trend in underpredicting at the top end.

Figure 6 presents the comparison of the modelled and observed **ground level total sulphur in air**. This is done by adding the SO_2 and SO_4^{2-} after converting them to their sulphur equivalent. This plot shows a slight overprediction. Most regions show points on both sides of the 1:1 line.

Figure 7 gives the comparison of the modelled and observed **SO_4^{2-} concentration in precipitation**. The scatter in these data is large. Nevertheless, the mean of the observed agrees with the mean of the modelled values. In other words, there is little systematic bias.

Analyses were also made on the ground level NO_2 and nitrate concentrations in air and the nitrate concentrations in precipitation. The NO_2 in air is slightly underpredicted and the nitrate in air overpredicted. These air nitrogen species show less consistent behaviour in terms of under- and overprediction than the corresponding sulphur species. These also show more scatter. The wet nitrate shows a slight underprediction with even larger scatter than the corresponding sulphur concentrations in precipitation. Since measurements of nitrogen species concentration cannot be made with very high accuracy, we will focus only on the sulphur species.

3. Interpretation of Model Performance

The EMEFS is the first time ground level air sulphur concentration has been evaluated extensively. A major explanation needed for the performance is the overprediction of SO_2 in air and underprediction of SO_4^{2-} in air.

A plot of the temporal trends of the ground level air SO_2 and SO_4^{2-} concentrations (see Figure 8 for Region 5) shows that the temporal trends of both species are captured by the model. The same level of agreement between modelled and observed data is seen for other regions. Inspection of the meteorology of Region 5 reveals that an increase in the concentration is associated with a dry period while a decrease is associated with precipitation which scavenges the pollutants. For the regions away from major sources, the wind advecting the pollutants into and out of the region also contributes to the fluctuation. Thus, the above performance suggests that the meteorology responsible for transport is reasonable. So the explanation may lie in the chemistry.

The performance of the sulphur species indicates that the total amount of sulphur in the first level is approximately correct and that SO_2 is converted to SO_4^{2-} too slowly. This can be due to two reasons:

1. A missing mechanism: Studies in Europe (e.g. Ruprecht and Sigg, 1990) have suggested that SO_2 can be converted to SO_4^{2-} in fog at a much faster rate than in dry air. Fog acts like a cloud as an aqueous-phase medium for rapid SO_2 oxidation. A preliminary study on the first 12 days of the simulation period based on weather maps shows that fog is prevalent. ADOM does not handle fog at present. However, that study also shows that fog cannot be the sole explanation.

2. Inaccurate Oxidant Chemistry: Preliminary comparison at one point in Region 2 of modelled and aircraft measured vertical oxidants (H_2O_2) profiles indicates that H_2O_2 is significantly underpredicted by the model throughout the entire column of the atmosphere. This will limit the rate at which SO_2 is converted to SO_4^{2-} both in air and in cloud.

The above suggestions are currently under investigations.

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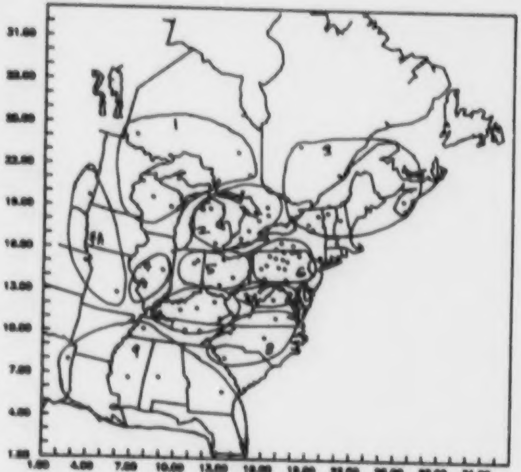
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Figure 1. The ground based monitors of the EMEFS with the outline of the nine regions for our evaluations.

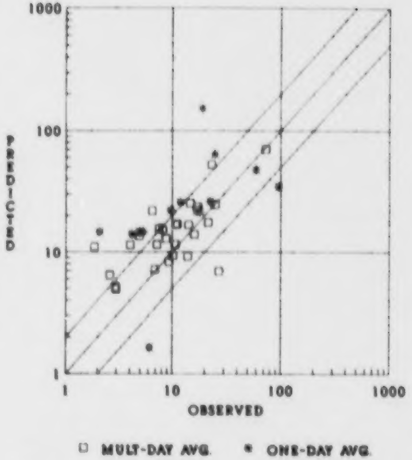

Figure 3. Comparison of event averaged observed and modelled sulphate concentration (μM) in precipitation for the winter study. The diagonal is the 1:1 line and the line on each side is the factor of 2 line.

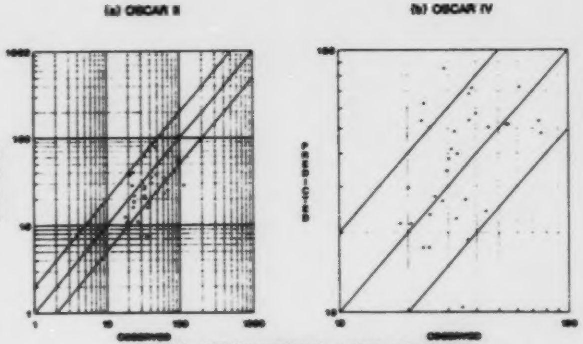

Figure 2. ADOM's predicted vs observed sulphate concentration in precipitation (μM) during OSCAR II (a) and OSCAR IV (b). The diagonal is the 1:1 line and the line on each side is the factor of 2 line.

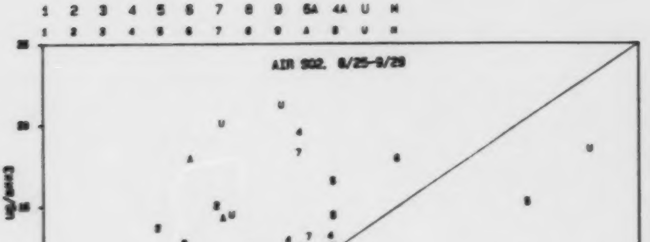

Figure 4. Modelled vs. observed ground level concentration for SO_2 for August 25 - September 29, 1988 for EMEFS.

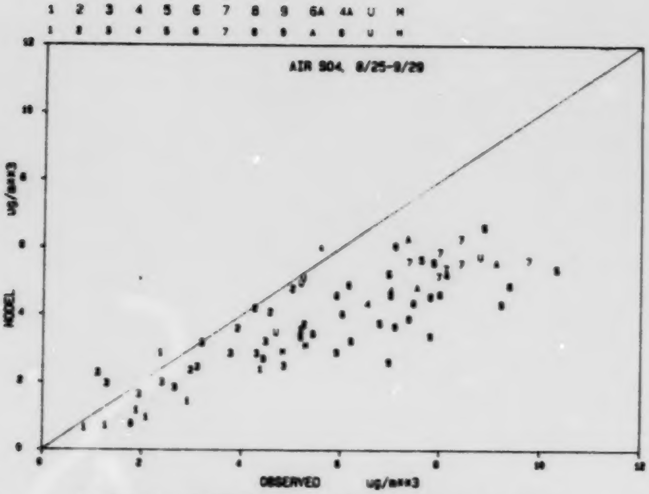

Figure 5. Modelled vs. observed ground level concentration for sulphate for August 25 - September 29, 1988 for EMEFS.

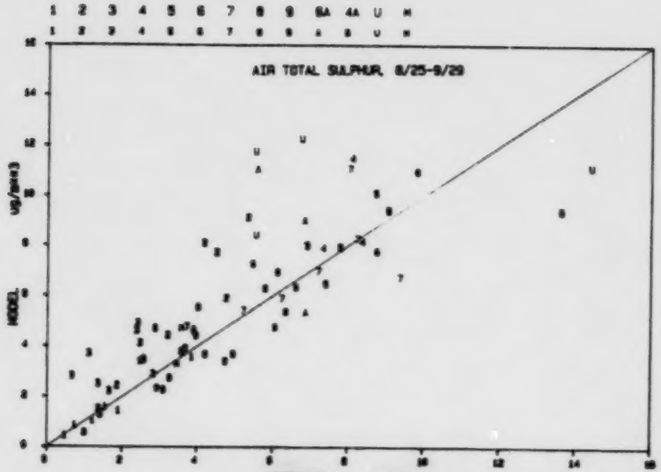

Figure 6. Modelled vs. observed ground level concentration for total sulphur for August 25 - September 29, 1988 for EMEFS.

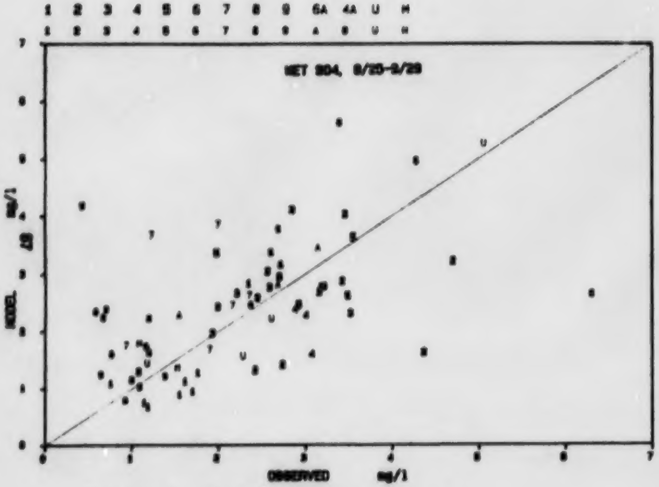

Figure 7. Modelled vs. observed concentrations in precipitation for August 25 - September 29, 1988 for EMEFS.

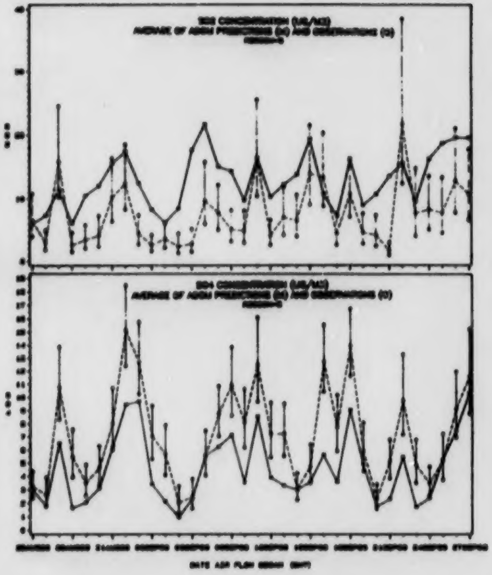

Figure 8. Time trends of ground level concentration for SO_2 and SO_4^{2-} during EMEFS.

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Modeling the influence of topography on dense gas dispersion

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1 Introduction

Topography, in the form of general slope, isolated hills, or more complex terrain, will alter or divert a dense gas cloud or plume. The topography may enhance plume dilution and divert the plume away from regions of elevated terrain; or, the dense plume may be channeled into valleys or low-lying areas and then be protected from the diluting influence of the ambient flow. These important effects are not included in the models currently used to predict the dispersion of a dense gas cloud for risk assessment or emergency management. The principal aim of this project is the development of numerical modeling techniques, based on rational physical principles, for incorporating the effect of topography in dense gas dispersion models.

This paper presents a review of some of the existing background theory and literature relevant to this problem. There is extensive treatment of the interaction of topography with buoyancy influenced flows in the geophysical literature, but little use has been made of this information source for dense gas dispersion. The report on which this paper is based (Ramsay & Britter 1990) provides a more extensive review of previous work on topographic effects on dense gas dispersion.

2 Gravity currents

The Front

The leading edge of a gravity current forms a frontal zone with a sharp interface between the dense fluid of the current and the surrounding ambient fluid. A characteristic 'head' which is deeper than the following flow is usually formed at the front. The raised head is a zone of breaking waves and intense mixing which plays an important role in the dynamics of the gravity current. A definition sketch for a gravity current is shown in Figure 1.

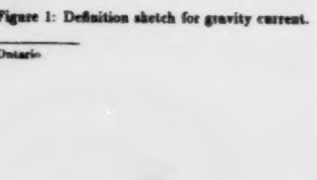

Figure 1: Definition sketch for gravity current.

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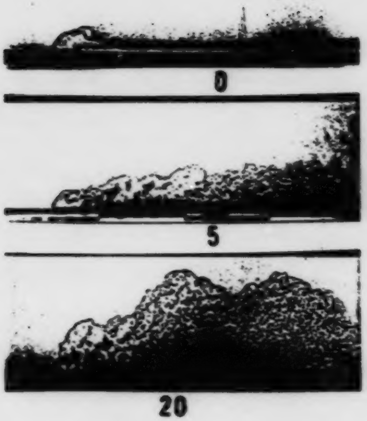

Figure 2: The effect of slope on the form a the gravity current head for slopes of 0°, 5° and 20° (from Britter & Linden 1980)

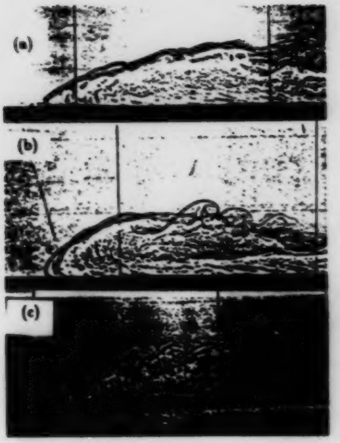

Figure 3: The effect of ambient flow on the form of the gravity current head (a) head wind (b) calm (c) tail wind (from Simpson 1987)

Gravity currents on slopes

A gravity current on a sloping surface is appreciably different from that on a horizontal surface. For a given rate of flow of a dense fluid on slopes of a few degrees to 90° slope there is a nearly constant front velocity. The front velocity is found to be about 60% of the mean velocity of the following flow. That is, about 40% of the flow arriving at the front is mixed into the head.

Figure 2 shows three different forms of the head of a gravity current: on a horizontal surface and on slopes of 5° and 20°, respectively. The head volume increases, both by direct entrainment and also by addition from the following flow. There is little variation of the front speed with slope because, although the gravitational forces increase with slope, so does the entrainment, both into the head and into the flow behind it.

Effect of ambient flow

The profile of the head of a gravity current and the velocity of the front are very sensitive to any opposing or following flow in the environment. These head- and tail-flow effects on the gravity current moving on a horizontal surface have been examined by Britter & Simpson (1978).

The experiments show that with a head wind the head profile is longer and the nose height lower than in the calm case previously described. With a tail wind the head is shorter and the node height is larger. The three different forms are shown in Figure 3.

3 Effect of slope

The classical analysis of Ellison & Turner (1959) is based on the theory of plumes with an entrainment function dependent on the overall stability characterised by an overall Richardson number. Several assumptions are made, the most important being: the turbulence is in a state of local equilibrium; the influence of the Reynolds number and the Prandtl or Schmidt number may be ignored; variations in density may be neglected in the inertial terms (i.e. the Boussinesq approximation); and, the pressure is hydrostatic normal to streamlines.

This flow is of considerable interest because it is a flow in which the density difference gives rise to both the flow down the slope and a reduction in entrainment through the density gradient strongly inhibiting turbulent mixing. That is, a flow in which the dynamics are self-limiting.

The characteristic plume velocity U and length h are defined by

$$Uh = \int_0^\infty U\,dy; \qquad U^2h = \int_0^\infty U^2\,dy \tag{1}$$

A scale for the local density difference $\Delta\rho$ is given by

$$g'Uh = g'_0 q_0 = \text{constant} \tag{2}$$

where $g' = g(\Delta\rho/\rho_a)$ and q_0 is the volume flux per unit width at the source which has density difference $\Delta\rho = \rho_{-}\rho_a$ (the subscript 0 indicates conditions at the source). Thus the basic momentum equation is

$$\frac{d}{dx}(U^2h) = -C_DU^2 - \frac{1}{2}\frac{d}{dx}(S_1g'h^2\cos\theta) + S_2g'h\sin\theta \tag{3}$$

where the terms on the right are the surface shear, hydrostatic pressure and downslope gravitational acceleration, respectively, and

$$E = \frac{1}{U}\frac{d}{dx}(Uh) = \frac{U_e}{U} \tag{4}$$

The shape factors S_1 and S_2 are given by

$$S_1g'h^2 = \int_0^\infty 2g\frac{\Delta\rho}{\rho_a}y\,dy; \qquad S_2g'h = \int_0^\infty g\frac{\Delta\rho}{\rho_a}\,dy \tag{5}$$

and are typically 0.25 and 0.75, respectively. The surface shear stress is $\tau_0 = \rho C_DU^2$.

The entrainment function E is assumed to be a function of the overall Richardson number Ri

$$Ri = \frac{g'h}{U^2}\cos\theta = \frac{g'_0q_0}{U^3}\cos\theta \tag{6}$$

It was shown by Ellison & Turner (1959) that the general solution rapidly approaches the x−independent solution

$$E = \frac{dh}{dx} = \frac{S_2Ri_n\tan\theta - C_D}{1.5S_1Ri_n} \tag{7}$$

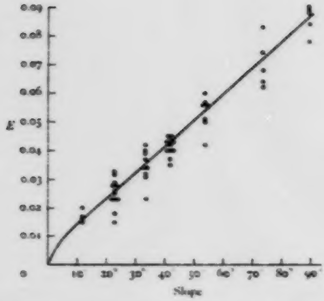

Figure 4: Measurements of entrainment into an inclined plume as a function of slope (from Ellison & Turner 1959).

where Ri_n is the x–independent solution of $Ri(x)$, and is termed the 'normal' Richardson number. That is, for any slope Ri_n is a constant and the velocity U is not a function of x but is proportional to $(g'_0 q_0)^{\frac{1}{3}}$. It is immediately apparent from this equation that the behaviour of the inclined plume is independent of the wall stress at large slope. The rapidity with which the flow approaches the state at which $Ri = Ri_n$ suggests that the flow will also rapidly adjust to slope changes.

Further progress requires using experimental data which links two of E, Ri_n and θ. Although the $E - Ri$ correlation is more basic, the $E - \theta$ correlation is often used. These correlations have been the subject of much study and are central to the discussion which follows. There is still considerable doubt as to the correct correlations (see Delft Hydraulics Laboratory 1974).

4 Entrainment function

The experimental results on entrainment by Ellison & Turner (1959) may be approximated by $E \simeq 10^{-3}\theta$ for θ in degrees although data was only collected for angles greater than 10°. The variation of velocity (which is independent of x) with slope was from $1.5(g'_0 q_0)^{\frac{1}{3}}$ at 10° to $2.15(g'_0 q_0)^{\frac{1}{3}}$ at 90°. Pedersen (1980) presents these entrainment results together with more extensive laboratory and field data and suggests $E = 1.2 \times 10^{-3}\theta$ for all angles greater than 6×10^{-3} degrees.

Entrainment at an interface appears to be determined by two distinct, yet not independent, mechanisms: the instability and subsequent mixing of the interface (i.e. a flow dependent on interface parameters; and, entrainment as a result of turbulence generated near the lower boundary propagating (diffusing) to the interface. The former is more relevant at large slopes while the latter only becomes significant for small slopes.

There is considerable evidence that a velocity/density interface is unstable when the gradient Richardson number is less than a critical value but stable above this critical value (see, for example, Sherman, Imberger & Corcos 1978). With regard to the mixing as a result of turbulence generated at the interface it seems agreed (see Linden 1979) that the interface thickens until a limit is reached at which the interfacial Richardson number equals some critical value. The problem is more difficult when the mixing allows conditions on one or both sides of the interface to be altered by the mixing. The two dimensional plume on the slope falls into this category.

A further useful experiment is the free surface jet studied by Townsend (1967) and Ellison & Turner (1959). This experiment isolates entrainment due to interfacial instability from that due to boundary effects.

The basic equations for the continuous, steady, surface jet are:

$$\frac{1}{U}\frac{d(Uh)}{dx} = E \tag{8}$$

and

$$\frac{d(U^2h)}{dx} + \frac{1}{2}\frac{d(S_1 g' h^2)}{dx} = 0 \tag{9}$$

which integrates to

$$U^2h + \frac{1}{2}S_1 g' h^2 = \text{constant} \neq f(x) \tag{10}$$

This can be written as

$$\frac{h(1 + .5S_1 Ri)}{Ri^{\frac{1}{3}}} = \text{constant} \neq f(x) \tag{11}$$

From these experiments Ellison & Turner (1959) were able to deduce the variation of E with the Richardson number. E decreased from about 0.075 at $Ri \simeq 0$ to zero at a critical Richardson number of about 0.8. Koh (1971) supports this result and suggests the empirical form

$$E = 0.075\left[2\left(1 + \frac{Ri}{0.85}\right)^{-1} - 1\right]^{1.75} \tag{12}$$

Longuett-Higgins & Turner (1974) use the form

$$E = \frac{0.08 - 0.1Ri}{1 + 5Ri} \tag{13}$$

The other source of mixing is from turbulence generated away from the interface. The simplest and most common example of this would be where the turbulence is generated by the shear at a nearby rigid boundary. Dimensional analysis would suggest that

$$E = \frac{U_e}{U} = f\left(\frac{g'h}{U^2}\right) \tag{14}$$

where g' characterises the density difference across the interface, and h characterises either the distance from the boundary to the interface or the scale of the turbulence.

Lofquist (1960) studied the entrainment rates into flowing underlayers under conditions where interfacial instability is small. The literature survey carried out by the Delft Hydraulic Laboratory (1974) fitted Lofquist's data with

$$\frac{U_e}{U} \simeq 10^{-3}\frac{U^2}{g'h} \simeq 10^{-3}Ri^{-1} \tag{15}$$

although a coefficient of 5 × 10^{-4} is as good a fit to the data. At large Richardson number, Hansen (1975) and Hamblin & Carmack (1978) suggest that $U/U_e \simeq 2 \times 10^{-3}Ri^{-1}$, a result similar to Lofquist's.

Large scale data are rare but Hebbert *et al* (1979) supply information from a density inflow into the Wellington reservoir. They estimate $E = U_e/U \simeq 1.9 \times 10^{-4}$ when $Ri \simeq 17.4$. A coefficient of 2 in the above equation requires $C_D \simeq 0.014$, which is not an unrealistic value. Note that the use of $E \simeq 1.2 \times 10^{-3}\theta$ gives (with $\theta \simeq 0.06°$) $E \simeq 7.4 \times 10^{-5}$.

When Ri_* is very large and interfacial instability is weak, or zero, several authors argue that the result should be correlated in the form $E \propto Ri_*^{-1}C_D^{\frac{1}{2}}$ bringing out the explicit dependence on the wall shear stress.

Fischer *et al* (1979) argue that when the shear production is negligible ($Ri > 0.8$) then

$$E = CC_D^{\frac{1}{2}}\frac{U^2}{g'h} \tag{16}$$

That is

$$E = CC_D^{\frac{1}{2}}Ri_*^{-1} \tag{17}$$

with $C = 3.2$ given by the field experiments of Elder & Wunderlich (1972) and Hebbert *et al* (1979).

Lofquist (1960) gave $(u_*/U)^2 \simeq 5 \times 10^{-3}$ for his experiments. That is,

$$\frac{U_e}{U} \simeq 0.10\left(\frac{g'h}{u_*^2}\right)^{-1} \tag{18}$$

or

$$\frac{U_e}{u_*} \simeq 1.4\left(\frac{g'h}{u_*^2}\right)^{-1} \tag{19}$$

Thus

$$E = 1.4C_D^{\frac{1}{2}}Ri_*^{-1} \tag{20}$$

Kato & Phillips (1969) and Kantha, Phillips & Azad (1977) studied a constant stress experiment and found coefficients of 2.5 and 5.0 in two different experiments, the first using a continuous stratification and the second a two-layer density stratification, the coefficients referring to the correlation $U_e/u_* \propto (g'h/u_*^2)^{-1}$

Although there is still uncertainty about the relevant entrainment function, we assume that E is a known function of C_D and Ri in the following discussion. For example, Figure 5 suggests a typical combination of $E - Ri$ using the Ellison & Turner surface jet results at small Ri_* and $E \propto C_D^{\frac{1}{2}}Ri_*^{-1}$ at $Ri > 1$.

A final cautionary note is required out he correlation of E with $C_D^{\frac{1}{2}}Ri_*^{-1}$. It is often uncertain as to what C_D is meant to represent. Typically C_D is the drag coefficient $(u_*/U)^2$ for a particular surface with non-stratified flow. However, it may be easily shown that $C_D = f(Ri)$, although this dependence is normally neglected. Carson & Richards (1978) estimate that for the atmospheric boundary layer C_D is no larger than 3 × 10^{-4}

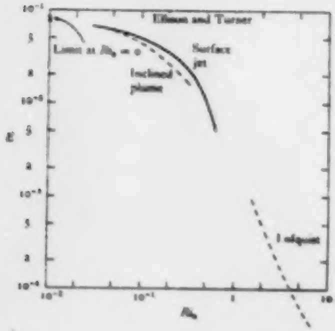

Figure 5: Rate of entrainment into a turbulent stratified flow as function of overall Richardson number (from experiments of Ellison & Turner (1959) and Lofquist (1960).

regardless of surface roughness for $Ri > 0.3$. Little difficulty arises provided all correlations are based on what C_D would be for the same mean velocity but $Ri = 0$.

The drag coefficient C_D includes the shear stress at the rigid surface and the (non-entraining) shear stress at the interface. The interfacial shear stress is small and negligible compared with the shear stress at the surface (Delft Hydraulic Laboratory 1974).

5 Effect of ambient flow

Ellison & Turner (1959) considered theoretically the interaction of a two-dimensional line source on a slope with a moving ambient up or down a slope. Their analysis is limited to cases where: the moving ambient is non-turbulent; and, the ambient either opposes the buoyancy driven motion or the ambient flow is smaller than the buoyancy driven flow when they are in the same direction. When the ambient fluid is dragging the plume forward Ellison & Turner (1959) argue that the entrainment may have a different dependence on Ri.

If U is the plume velocity relative to the ambient velocity U_a then

$$g'(U + U_a)h = g'_0 q_0 = \text{constant} \tag{21}$$

$$\frac{dh(U + u_a)}{dx} = E|U| \tag{22}$$

$$E = f(Ri) = \frac{g'_0 q_0 \cos\theta}{U^2(U + U_a)} \tag{23}$$

and

$$\frac{d}{dx}[(U + U_a)Uh] = -(U + U_a)^2 C_D \operatorname{sgn}(U + U_a) + S_2 g' h \sin\theta - \frac{1}{2}\frac{d}{dx} g' h^2 S_1 \cos\theta \tag{24}$$

Arguing that the flow rapidly adopts a 'normal' state in which

$$\left(1+\frac{1}{2}S_1 Ri\frac{U}{U+U_a}\right)E = S_2 Ri\tan\theta - C_D\frac{(U+U_a)^2}{U^2}\operatorname{sgn}(U+U_a) \tag{25}$$

Ellison & Turner (1959) obtain numerical solutions for the plume velocity $(U+U_a)/(g_0'q_0)^{\frac{1}{3}}$ as a function of $U_a/(g_0'q_0)^{\frac{1}{3}}$ (Figure 6). It is useful to note that the relevance of U_a may be determined by comparing it with $A = g_0'q_0$.

The curves in Figure 6 could be simply obtained by further numerical computation for other slopes and C_D, however, some of the limits are useful and easily obtained.

When $C_D = 0$ then

$$\left(1+\frac{1}{2}S_1 Ri\frac{U}{U+U_a}\right)E = S_2 Ri\tan\theta \tag{26}$$

If U and U_a are in the same direction and the slope is not very small $1+\frac{1}{2}S_1 Ri\frac{U}{U+U_a} \ll 1$ and, thus, $Ri = \frac{E}{S_2\tan\theta}$. This solution is such that the ambient velocity is simply added to the plume velocity in the absence of the ambient flow. A similar result holds when the ambient flow opposes the buoyant velocity. Dilution of the plume is reduced by a factor $\frac{U}{U+U_a}$ in the former case and enhanced by $\frac{U}{U+U_a}$ in the latter case.

A further particularly useful result is the ambient velocity required to reverse the buoyant flow of the plume. This is only a weak function of C_D and typically $U_a/(g_0'q_0)^{\frac{1}{3}} \sim 3-4$ increasing with slope.

Britter (1980) estimates that an ambient flow much greater than twice the leading edge velocity will stop the motion of the cloud. As the downslope velocities are not greatly enhanced by an increased slope, the upwind ambient velocity required to reverse the cloud is not greatly affected by the slope. This argument is consistent with Ellison & Turner's (1959) calculations and experiments.

No calculations or systematic experiments are available for anything other than the simple two-dimensional line source on a constant slope, however they may be obtained subject to the previous assumptions.

For a point or area continuous source it can be argued, without recourse to analysis, that the plume will not travel further against the ambient whenever $U_a/(g_0'\frac{Q_0}{w})^{\frac{1}{3}}$ exceeds 3-4 where w is the local width of the plume. This would seem to be a useful criterion for determination of the upwind distance that a plume might travel.

For the instantaneous source a similar argument would suggest that the cloud will not travel against the ambient flow unless, in the absence of the ambient flow, its velocity is more than about twice that of the ambient velocity.

Note also that significant upwind (downslope) travel is possible if the material does not spread laterally (e.g. if it is channeled into a small valley).

6 Conclusions

Topographic features that are small compared with the size of the release may be considered in much the same way as buildings or structures but without any substantial flow separation unless the topography is very abrupt. The shallow water equations are useful here (Lamb & Britter 1984, Lee & Meroney 1988). When the topographic feature is large compared with the scale of the release, the topography reduces to the

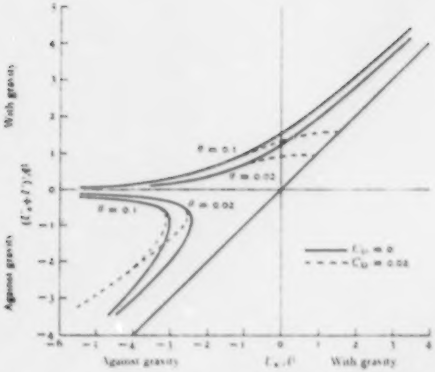

Figure 6: Calculations of the velocity of an inclined plume entraining a moving ambient flow (from Ellison & Turner 1959).

local slope. Somewhat surprisingly, the downslope velocity of a dense fluid released on a slope under calm conditions is not a strong function of the slope.

Broadly, three characteristic velocities are relevant: the ambient wind velocity; the buoyancy generated velocity found on flat terrain; and, the buoyancy generated velocity found on slopes (downslope). The latter two velocities both scale on $(g'h)^{\frac{1}{2}}$. As the coefficient in the expression for the slope flow is only a weak function of slope, the slope will have an effect on the clouds for which any buoyancy generated velocities are relevant. However, the flow development times may differ. For example, the instantaneous release might initially spread radially, then develop a bulk downslope flow, before finally being diluted and swept upslope by an ambient flow.

When the wind is upslope, the cloud widens and its dilution is enhanced. When the wind is downslope, the cloud is narrower and the dilution is decreased. The variation of the lateral growth of the plume results from the effective summation of the wind and the buoyancy induced motion down the slope. The entrainment is influenced by the velocity shear and will therefore be enhanced by an upslope wind and reduced by a downslope wind.

A distinctly different topographic influence occurs when the topography alters the velocity field within the cloud which is dispersing. Britter & Snyder (1988) found this to be more important than the direct effect of the slope on the cloud.

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A8

IGNITION STUDIES OF SELECTED EXPLOSIVE MIXTURES OF GASES AND DUSTS EMITTED FROM CEMENT KILNS

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Abstract: The gas compositions and the dust loadings of two cement plants were investigated. The samples were taken at the inlet and the outlet of the electrostatic precipitators and then analyzed on a gas chromatograph. The measured gas concentrations were used as a basis for flammability tests in order to verify or correct existing safe operation limits for the precipitators.

Two sets of flammability tests were conducted using a modified version of the 20 litre chamber designed by the U.S. Bureau of Mines. In the first set the lean limits of different clean gas mixtures which are assumed to be present under upset operating conditions were determined. In the second set the amount of cement dust necessary to render an explosive clean gas mixture inert was examined.

The results of the flammability tests showed that the measured exhaust gas composition was well in the safe range. Under upset conditions however, the gas composition could be explosive and in most cases the amount of dust present in the precipitator exhaust gas would not be sufficient to prevent an ignition of the gas.

I. INTRODUCTION

The operation of cement plants generates a considerable amount of cement dust which generally is collected by means of electrostatic precipitators (ESP). Inside the cement kilns, the calcination process is accompanied by the formation of carbon monoxide, hydrocarbons and other combustible gases. During transient conditions of the process, these gases may form explosive mixtures which could be ignited by the high energy sparks in the ESP. To prevent such hazardous conditions to develop, the kiln emissions of carbon monoxide and oxygen are continuously monitored by the cement industry. If an impending or already formed explosive mixture is detected, the electrostatic precipitators are immediately de-energized to prevent any sparks. The decision to shut down the precipitators, currently, is premised on very safe limits for allowable concentrations of combustible gas, without taking into account the unknown influence of substantial concentrations of cement dust present in the kiln exhaust gas. The scope of the investigation was to define new safety limits to minimize the number and duration of the power-outs of the precipitators. The paper includes analyses of actual exhaust gas samples from cement kilns and results from flammability test conducted on representative clean gas mixtures and various gas-cement dust mixtures.

II. COMPOSITION OF CEMENT KILN EXHAUST GAS

Kiln exhaust gas and dust loading samples were collected at two cement plants, each running different process streams. Two sets of 12 samples each were collected at various times at both the inlets and the outlets of the electrostatic precipitators. Each sample was analyzed for its gas composition using a gas chromatograph.

The dust loading was measured using thimble filters in which the dust was collected for a specified time period. Table 1 shows a summary of the average gas compositions and dust concentrations. In all cases, the variation of the gas concentrations was within 7% of the mean. No test was conducted under upset conditions in the process stream, so the found results provide a good indication of the background gas concentrations and the dust loadings under normal operating conditions. The results compared well with reference values estimated by the plant personnel.

Table 1: Kiln exhaust gas composition and dust loadings

Sample #	Process	CO_2	O_2	N_2	CO	H_2	UBHC	Dust loading (g/m³)
Plant 1, A	Inlet	29.5	3.6	66.7	0.13	< 0.02	< 0.06	32.7
Plant 1, A	Outlet	26.0	4.8	65.6	0.098	ND	ND	6.7
Plant 1, B	Inlet	21.4	7.4	ND	0.15	ND	ND	not taken
Plant 1, B	Outlet	not taken						
Plant 2, A	Inlet	24.8	6.1	64.0	0.031	ND	ND	314.1
Plant 2, A	Outlet	23.1	6.5	63.3	0.014	ND	ND	< 15.8
Plant 2, B	Inlet	24.9	6.1	63.4	0.026	ND	ND	551.2
Plant 2, B	Outlet	24.6	6.4	63.9	0.031	ND	ND	< 2.8

The results in Table 1 indicate that the exhaust gas of both cement plants contain typically 25% CO_2 and 63% N_2 at either inlet and outlet of the precipitator. The concentration of CO varied considerably from 0.1% in Plant 1 to 0.03% in Plant 2. Concentrations of H_2 and unburned hydrocarbons (UBHC), the latter one mainly composed of methane, exhibited some variability with time, but were present only in very small concentrations under normal operating conditions. In Plant 2, the O_2 concentration was typically 6%, but in Plant 1 it changed from 4-7.5% between samples A and B. This was due to substantial modifications in the process stream so sample B is thought to be most representative for normal operating conditions in Plant 1. A comparison with published explosion limits for single gases indicated that a mixture containing any one of the flammable gases at these concentrations would not ignite in the electrostatic precipitator [1].

Representative dust loadings, as shown in Table 1, lie in the range from 30-550 g/m³. The literature suggests that for volatile dusts, dust-air mixtures with loadings of 100 g/m³ could ignite under certain conditions, while loadings of 10-80% inert dust could suppress explosion even for very high ignition energies [2]. Thus, it was decided to test the full rage of dust loadings measured in the cement plant kiln exhaust and to extend the range depending on the initial results.

III. FLAMMABILITY TESTS OF KILN EXHAUST GASES

A. The Experimental Apparatus

The experimental apparatus used to test the flammability of representative clean gas and gas-dust mixtures is shown schematically in Figure 1. It was comprised of the explosion chamber, the associated gas handling system, a spark generating apparatus to ignite the gas and two transducers to detect an explosion. The chosen explosion chamber was a modified version of the 20 litre test chamber designed by the U.S. Bureau of Mines [3], shown in detail in Figure 2. Its volume was 23.5 litres. The original chamber has been shown to produce repeatable measurements of minimum ignition energies for gases, dusts and gas-dust mixtures [2,3].

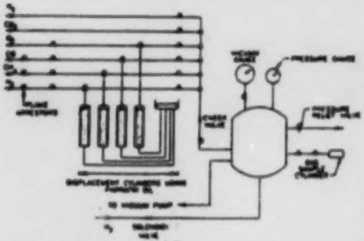

Figure 1: Schematic of the explosion chamber and associated gas handling system

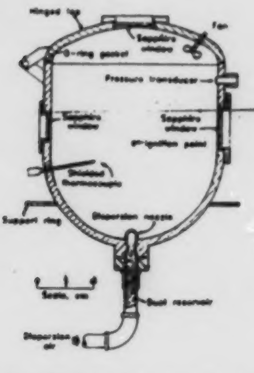

Figure 2: Details of the explosion chamber showing the instrumentation

The gas-dust mixture was ignited by means of a custom electric spark apparatus, consisting of a high voltage power supply and a variable capacitor unit. First the capacitor was charged to the appropriate voltage and then discharged between two sharp needle points to generate the spark.

To detect an explosion, the test chamber was equipped with a pressure transducer and a shielded thermocouple which were connected to a storage oscilloscope.

For each test, the chamber was evacuated, then purged with N_2, evacuated again and filled with the inert gases by partial pressure and the flammable gases by using displacement columns. Thorough mixing was accomplished by the filling procedure and was further enhanced using a fan inside the chamber. The final gas compositions were cross-checked using a batch gas sample that was analysed on the gas chromatograph. No major discrepancies between the target and achieved gas compositions were noted.

1) Characterization Of The Apparatus: The operation of the explosion chamber was tested by running a series of explosions using H_2/air mixtures with N_2 as the diluent. It was found that explosions occurred for H_2 concentrations greater than 6% and less than 32% with O_2 concentrations of 7% and 6% respectively. These values correspond well with those found in the literature [1], indicating that the explosion vessel was operating correctly.

B. Flammability Of Gas Mixtures Without Dust

Two separate sets of flammability tests with clean gas mixtures were carried out. The initial one was used to determine wether the typical exhaust gas in the precipitator was explosive or not. No one of the gas compositions listed in Table 1 ignited, even with spark energies of 3-5 J. This was expected since, under normal operating conditions, the probability of an explosion in the cement plant is very low.

The danger in operation occurs when the process undergoes an upset in conditions since transients might increase the concentrations of flammable gases by as much as 50 times. This would increase the concentrations of CO to 7.5%, of H_2 to 1% and of CH_4 to 3%. It was not known whether this mixture would explode, since the flammability limits for many multiple gas mixtures have not been recorded previously. To test the flammability limits of gas mixtures similar to those postulated for upset conditions, a composition of 25% CO_2, 8% O_2 and 1.5% CH_4 was chosen as a base mixture. The quantities of CO, H_2 and N_2 in the mixture were varied individually and in combination to find the lean flammability limits. For a mixture as above but also containing 2.5% CO, the amount of H_2 was increased from 0.1% to greater than 30% (with corresponding decrease in the quantity of N_2). In no case did the gas mixture explode. A second mixture as above, but with 1% H_2 was used to test varying proportions of CO and N_2. It was found that explosions occurred for mixtures containing greater than 10% CO. When the percentage of H_2 was increased to 3%, explosions occurred in mixtures with only 7.5% CO. The results are shown with other published data in Figure 3. The agreement is good and clearly indicates the sensitivity of flammability limits to concentrations of all flammable gases, particularly when they are found combined in a mixture.

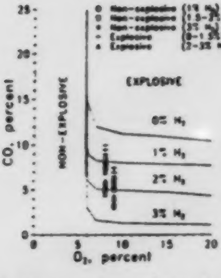

Figure 3: Comparison of present results with previously published flammability data [4]

C. Flammability Of Gas-Dust Mixtures

The next series of experiments were conceived to test the flammability of gas-dust mixtures which were assumed to represent the kiln exhaust under upset operating conditions. In the four cases studied the concentration CO_2 and CH_4 was held constant at 25% and 1.5% respectively. The concentration of O_2 and H_2 was changed for each case to investigate the notional sensitivity of explosions towards these gases, and the amount of CO was varied to find the flammability limits. The N_2 was used to fill to make 100% mixture.

Once the lean limit was found for each case, the quantity of cement dust required to inert an explosive gas mixture was determined for incrementing CO levels. The type of cement dust was the same for all flammability tests described below. Its mean particle diameter was 4 μm with the 10% limit at 2 μm and the 90% limit at 12 μm.

1) Case 1: 8% O_2 and 1.5% H_2: In the first set of flammability tests with clean gas and gas-dust mixtures a base gas consisting of 25% CO_2, 8% O_2, 1.5% CH_4 and 1.5% H_2 was used. The amount of CO was varied and N_2 was added to make 100% mixture. The results of the tests are plotted in Figure 14 as concentration of CO in the clean gas mixture versus concentration of cement dust added to the mixture.

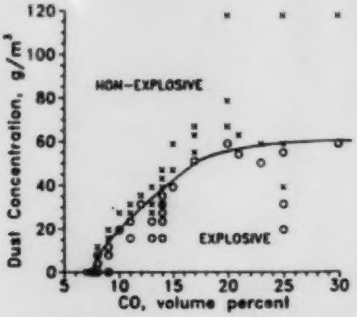

Figure 4: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 8% O_2, 1.5% CH_4, 1.5% H_2

The clean base gas exploded for CO concentrations greater than 7.5%, as can be seen from Figure 5. This is consistent with results obtained previously. For increasing concentrations of CO in the base gas mixture, it took increasing quantities of cement dust to render the gas mixture non-explosive, up to concentrations of approximately 17% CO. At this concentration of CO it took approximately 50 g/m³ of cement dust to suppress an explosion.

For concentrations of CO greater than 17%, an asymptotic limit appeared to had been reached where no more than 50 to 60 g/m³ cement dust was required to suppress an explosion up to concentrations of CO as high as 30%.

These results suggest that if the cement dust concentration was maintained above the apparent asymptote of 50 to 60 g/m³, the danger of an explosion in the cement plant precipitators could be reduced. Unfortunately, while this dust concentration is below the level measured at the inlet to the precipitators in Plant 2, it is substantially higher than the dust concentrations measured at the outlet to Plant 2 or at the inlet or outlet in Plant 1. Therefore, it can not be expected that the presence of the cement dust in the process stream would always render explosive mixtures of gases inert when the plant is operating under upset conditions.

2) Case 2: 8% O_2 and 3.0% H_2: The second set of flammability tests with clean gas and gas-dust mixtures was carried out using a base gas composed of 25% CO_2, 8% O_2, 1.5% CH_4 and 3.0% H_2. The amount of CO was varied and N_2 was added to make 100% mixture. The results of the tests are plotted in Figure 5 as the concentration of CO in the gas mixture versus the amount of cement dust dispersed in the gas mixture.

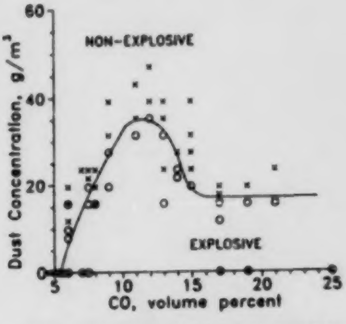

Figure 5: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 8% O_2, 1.5% CH_4, 3% H_2

Figure 5 shows that the clean base gas exploded for CO concentrations greater than 5%. In the range of 5% to approximately 12% CO, increasing quantities of cement dust were necessary to render the gas mixture non-explosive for increasing concentrations of CO. At the upper end of the range it took approximately 35 g/m³ of cement dust to suppress an explosion. For concentrations of CO greater than 12%, the quantity of dust required to suppress an explosion decreased sharply, reaching an asymptotic limit of 15-20 g/m³ for concentrations of CO greater than 16-17%.

Through comparison of Figure 4 and Figure 5 it can be seen that doubling the quantity of H_2 in the base gas (Case 2) increased the flammability of the clean gas mixture since it required CO concentrations of only 5% to cause an explosion in Case 2. In similar fashion to Case 1, it took increasing quantities of cement dust to render the mixture inert for increasing concentrations of CO. However, for the same concentrations of CO as in Case 1, it generally took more dust to suppress an explosion for the base gas used in Case 2. This suggests that increases in the quantity of H_2 in the base gas lead to explosions that are more difficult to suppress with the cement dust.

In sharp contrast to the results in Case 1, for Case 2 it appeared that with CO concentrations greater than 12%, the quantity of dust required to suppress explosion sharply decreased, reaching an asymptotic value much lower than that observed in Case 1. These trends and the value of the limit were completely unexpected, and may be due to scatter in the data resulting from the small number of verification tests performed at these high CO concentrations.

3) Case 3: 9% O_2 and 1.5% H_2: Since the explosion tests of the clean gas mixtures showed a high sensitivity towards the O_2 concentration, further tests were conducted on gas and gas-dust mixtures using a base gas composed of 25% CO_2, 9% O_2, 1.5% CH_4 and 1.5% H_2. The amount of CO was varied and N_2 added to make a 100% mixture. The results are plotted in Figure 6 with the CO concentration versus the quantity of cement dust added to the gas mixture.

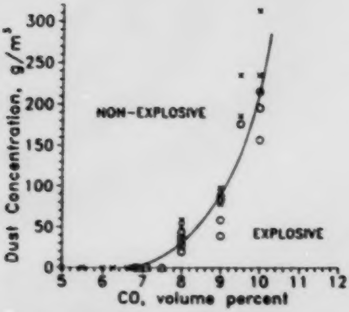

Figure 6: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 9% O_2, 1.5% CH_4, 1.5% H_2

It can be seen from Figure 6 that the clean base gas exploded for CO concentrations greater than 6.5%. For increasing concentrations of CO in the base gas mixture, it took greatly increased quantities of cement dust to render the gas mixture non-explosive. The results appeared to have an exponential rather than an asymptotic behaviour. This might have been due to the fact that the dust dispersion mechanism of the experimental apparatus did not operate repeatably for cement dust loadings greater than 350 g/m³ and a possible asymptotic region could not be reached.

A comparison of Case 1 and Case 3 indicates that if the content of O_2 in the base gas is increased from 8% to 9%, the quantity of cement dust required to suppress an explosion rises by approximately a fivefold for similar concentrations of CO. All the quantities of dust required to suppress explosions in Case 3 are well above the concentrations that were measured at the inlet or outlet of cement Plant 1 or at the outlet of Plant 2 and, when a concentration of 10% CO is reached, they are approaching those measured at the inlet of Plant 2.

4) Case 4: 9% O_2 and 3.0% H_2: The final set of tests was conducted on gas and gas-dust mixtures using a base gas of 25% CO_2, 9% O_2, 1.5% CH_4 and 3.0% H_2. Like for the previous tests, the amount of CO was varied and N_2 added to make 100% mixture. The results are plotted in Figure 7 as concentration of CO in the gas mixture versus amount of cement dust dispersed in the gas mixture.

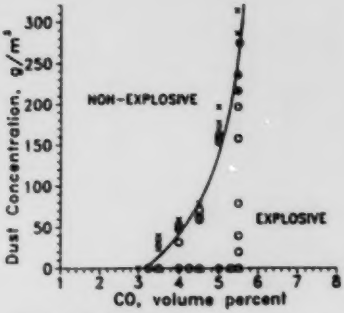

Figure 7: Results of flammability tests with clean gas and gas-dust mixtures using a base gas composed of 25% CO_2, 9% O_2, 1.5% CH_4, 3% H_2

From Figure 7, it is evident that the clean base gas exploded for CO concentrations greater than 3.0%. As in Case 3, for increasing concentrations of CO in the base gas mixture, it took greatly increased quantities of cement dust to render the gas mixture non-explosive. The curve is even steeper than the one in Case 3, as would be expected with the higher concentrations of H_2 present in the base gas. For a set of tests not shown, with concentrations of 7.5% CO, it was not possible to suppress explosion, even with dust loadings greater than 300 g/m³. No asymptote was apparent in the results of Case 4.

A comparison of Case 2 and Case 4 indicates that, for similar concentrations of CO, a 1% increase in O_2 concentration provides a mixture in which explosion cannot be suppressed, even with very large quantities of cement dust. The concentrations of cement dust which would be required to suppress explosion in mixtures containing even the lowest concentrations of CO found in these base gas mixtures are much higher than those measured at either the inlets or the outlets of the precipitators in Plants 1 and 2. With 9% concentration of O_2 in the base gas, then, the danger of explosion is very real, even for modest quantities of CO in the precipitator gases.

5) Observations: In all of the cases discussed above, only one type of cement dust has been used to determine the concentrations of dust required to suppress explosion in the base gas mixtures. It has been reported that results in flammability testing of gas-dust mixtures are dependent on both the composition and particle size of the dusts used in the experiments. In addition, the uniformity of dust concentration in gas-dust mixtures has been shown to influence flammability results.

In a independent set of tests, the effects of cement dust particle size on explosion suppression were tested by passing the dust through a fine sieve before dispersing it in the explosion chamber. Subsequently, it was found that 10-15% less dust was required to suppress explosion in a given gas mixture. The results should serve as a warning that the absolute concentrations given in this report are not universal limits on the quantities of cement dust that would be required to render an explosive gas mixture inert.

IV. CONCLUSIONS

1. Analysis of samples of kiln exhaust gases collected at Plants 1 and 2 indicated that, under normal operating conditions, the concentrations of flammable gases in the exhaust are well below those required to form an explosive mixture.

2. Under plant upset conditions, it is conceivable that explosive gas mixtures might be formed. Flammability tests of simulated exhaust gas mixtures without dust indicated that, while the explosion limits are very sensitive to the concentrations of CO and H_2 in the mixture, they are far more dependent on the O_2 concentration in the background gas.

3. Flammability tests of gas-dust mixtures with a single type of dust indicated that with 8% O_2 in the base gas, 50 g/m^3 of cement dust appeared always to render an explosive gas mixture inert, even when the CO concentration exceeded 20%. Unfortunately, this dust loading is higher than those normally encountered in the cement plant precipitators. Therefore, the presence of cement dust in the process stream should not be expected to suppress explosion in the precipitators when the plant is operating under upset conditions.

4. In all flammability tests, increasing quantities of H_2 in the base gas led to more explosive mixtures. Therefore, greater quantities of cement dust were required to suppress explosion in mixtures containing higher concentrations of H_2.

5. When the O_2 concentration in the base gas was increased from 8% to 9%, the flammability behaviour changed drastically. For small increases in CO concentration in the base gas, exponential increases occurred in the quantity of dust required to suppress explosion. If levels of 9% O_2 were ever reached in the kiln exhaust gases, the danger of explosion in the precipitator would be greatly increased, even with levels of CO as low as 5-7% by volume.

6. A series of short tests showed that the results obtained are dependent on the type and the size distribution of the cement dust and therefore the results of the tests must be applied with care.

7. In general, it takes high loadings of cement dust to effectively suppress explosion in a mixture of flammable gases that might be found in the cement kiln exhaust gases. Therefore, the presence of dust in the exhaust gas stream should not be expected to render an explosive gas mixture inert, particularly, for instance, at the precipitator outlet where the dust loading is usually quite small.

8. Since the flammability of the gases appeared to be more sensitive to CO and H_2 concentration than to that of UBHC (CH_4), monitoring the concentrations of these gases should remain a major part of the plant control operation.

9. The flammability of typical exhaust gas mixtures is highly dependent on the concentration of O_2 in the mixture, therefore the danger of explosion might be reduced by maintaining the exhaust gas O_2 concentration below about 6-7%, i.e., by minimizing leakage in the region of the precipitators.

10. If more detailed information was available on the upset conditions that occur in a specific cement plant, the results of this study might be more meaningfully interpreted for analyzing the possible explosion hazard.

VI. ACKNOWLEDGEMENTS

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A8

EVALUATION OF METHODS TO DETERMINE THE IMPACTS OF RESIDENTIAL WOODBURNING ON AMBIENT AIR IN ONTARIO

M.E. Yandle, C.S. Davis, D.L. Dougherty

Abstract

During the fossil fuel shortage of the mid seventies, the availability of fuel wood prompted a significant increase in the use of residential wood stoves and fireplaces in many North American and Scandinavian communities. In Ontario, an increasing number of residents have been using wood stoves to substitute or augment heating provided by other means, as well as using wood burning fireplaces.

The increased use of residential wood as a fuel has resulted in deterioration of ambient and indoor air quality is several areas. The most direct evidence of this deterioration has been the increase in ambient total suspended particulate and carbon monoxide levels especially in areas that have poor atmospheric dispersion conditions. The concern over the air quality impact of residential wood combustion (RWC) is heightened by the composition of the emissions which have proven to contain toxic and carcinogenic species of which the polynuclear aromatic (PNA) compounds are most important. The PNA compounds emitted may undergo atmospheric chemical reactions with nitrogen oxides and ozone to produce a further variety of compounds which are potentially toxic or mutagenic.

Investigation in the United States of areas of non-attainment of carbon monoxide (CO) and aerosols revealed the significant impact of the collective effect of residential wood combustion (RWC). Special studies to determine the air quality impacts of RWC were undertaken in several wood-burning states especially in the Pacific Northwest - Colorado, Washington, Oregon, Idaho, as well as in states such as Minnesota, Michigan, New York, Maine, North Carolina, New Hampshire and Vermont. As can be anticipated, results of these studies confirmed the necessity to adopt standards of stove efficiency. To complement these efforts, the emissions produced by woodstoves were investigated. Areas examined included: chemical composition, emission rates, and physical factors affecting the combustion process (moisture content, stove efficiency, etc.).

In Ontario, complaints regarding RWC emissions have been registered with municipal and regional government offices. The Ontario Ministry of the Environment has recognised the significance of the RWC sources in several communities and a study to investigate the potential impact of RWC sources on ambient air quality was undertaken by Concord.

The first phase of the study has reviewed and compiled current information regarding the environmental impact of residential wood combustion. In the future, areas of significant potential for adverse air quality impacts from RWC in Ontario will be studied in order to characterize the extent of the impacts and to determine the need for appropriate control and abatement policies and strategies.

Objectives

The objectives of the first phase were to search the relevant literature, review articles and reports, and to summarise the current status on the following topics:

- current emission regulations and abatement strategies;
- source characterization;
- sampling techniques;

- analytical techniques;
- airshed impact studies;
- atmospheric (chemical and phase stability); and
- data analysis and assessment methods (tracer methods, chemical mass balance, receptor modelling, multivariate methods, etc.).

The focus of this study was to gather relevant information and evaluate the technical merits of the past research efforts and to assess the potential for RWC impacts in Ontario and to recommend further action. The recommendations were based on an experimental design that will incorporate the most effective sampling and analytical methods to collect the optimum amount of information required to assess the RWC impacts and, where necessary, resolve contributions from similar sources. The intent of a subsequent investigation will be to quantify and document the effects of RWC in selected areas in Ontario.

Methodology

The relevant literature databases were searched and the pertinent articles and reports were obtained. The information was categorized into the areas of interest and was reviewed in the context of the objectives. Invariably, some documents impinged upon several topics, and articles of this nature were reviewed successively. The approach of the literature review was to provide a concise, focused evaluation of current technology, rather than an article by article review.

Review of Controls and Regulatory Strategies

Wood heating appliances are regulated by a wide variety of programs and provisions that either directly or indirectly impact upon the design, testing, performance and installation of the appliance with respect to air contaminant emissions. In several areas of the United States especially in the northwest, the increased use of residential wood heating appliances has forced many areas to develop and implement measures designed to regulate the amount of emissions produced by woodstoves. The measures fall into three categories:

1. the development of efficiency, design and emission codes and standards for wood burning appliances;
2. setting maximum permissible air pollution levels and installation regulations; and
3. control strategies and programs and non-regulatory activities.

Regulations promulgated have included:

- design and/or technology standards (woodstove certification requirements);
- emission standards for particulates, and in some cases carbon monoxide and/or opacity;
- voluntary and mandatory burning curtailment on days of poor air quality; and
- limitation of the number of installations.

Control strategies and programs vary and typically include one or more of the following elements:

- public education programs;
- voluntary burning curtailment;
- woodstove retrofits (with catalytic converters);
- certified woodstove replacements;

- firewood seasoning rules;
- weatherization of wood-heated homes;
- wood stove licensing; and
- incentive programs such as low interest or no interest loans, tax credits, preferred utility rates, rebates, etc. for replacement and or upgrading of units.

In early 1984, the Canadian Standards Association assembled a Committee to develop a comprehensive performance test standard for wood stoves. The Canadian Wood Energy Institute and the Department of Energy, Mines and Resources (EMR) triggered the formation of the Committee. Its mandate was two-fold: firstly, to develop test procedures designed to provide reproducible performance measures, and secondly, to assess whether performance testing should be voluntary or mandatory, and whether pass/fail criteria should be established.

The preliminary standard was developed and incorporated specific guidelines regarding test facilities, instrumentation, fuelling methods, testing procedures and, finally, the manner in which test results would be calculated for such key indicators as heat output, average stack temperature, burn time (duration of burn), appliance efficiency and emissions (Braaten, 1984). The preliminary standard however did not incorporate maximum emission nor minimum efficiency standards and was never promulgated. The Committee is currently revising the standard to incorporate both maximum emissions and minimum efficiency standards similar to U.S. EPA federal standards. A draft form of the revised standard was to be ready during the next Committee meeting in February 1990 (B. Wier, 1989). Some effort has been made by the Committee to harmonize development of the CSA standard with EPA.

Factors and Effects on Emissions

In all combustion processes, both physical and chemical factors (variables) affect the efficiency of combustion and also the emissions produced by the combustion process. As the number of variables affecting the conversion to energy increases, efficiency invariable decreases. Wood combustion is based on the most common exothermic process, in which carbon is oxidized to CO_2 by oxygen.

Wood consists of cellulosic material in which there are a wide range of oxygenated and hydrocarbon type organic compounds. Not surprisingly, alteration of the combustion conditions results in a myriad of byproducts including: carbon monoxide, particulate matter and a wide spectrum of organic species of which polycyclic aromatic hydrocarbon species (PAHs) are of greatest concern.

The factors that affect the combustion most are:

a) rate of oxygen supply - ventilation
b) rate of carbon supply - batch size, fuel composition, fuel type
c) temperature - stove characteristics, operating conditions

The other factor that affects the efficiency of combustion is temperature. These factors are further identified with respect to the characterization of emissions from residential woodstoves in the following paragraphs.

Fue [illegible]

Aside from the numerous varieties of wood fuels, commercially produced newspaper logs, cardboard logs, compressed wood (with and without binders), treated wood, peat and bituminous coal are used to fuel stoves on the North American continent. The conditioning process of these fuels is a significant factor in determining the efficiency of the heating device and the emissions produced.

In Ontario, alternate fuels used to heat residences generally are limited to a few species of woods, and are listed below.

REGION	WOOD TYPES USED
Northwestern Ontario	Birch, jack pine, spruce
Central Ontario	Sugar maple, birch
Eastern Ontario	Birch

While newspaper logs and cardboard logs are used occasionally for ornamental fires in fireplaces, these fuels are extremely high in price and, hence, are not used for prolonged, nor intensive fuel combustion. For these reasons, discussion of fuels will be limited to commonly available wood types.

Soft and hard wood types generally have different heating values due to different composition, structure and density. Total particulate emissions by fuel type have been found to very from 8.9 g/kg to 29 g/kg (Hartman and Rives, 1985). A typical emission rate for non-certified conventional woodstoves is around 20 g/kg (tested using Oregon/EPA Certification) (personal correspondence with J. Core). Fuel type effects also are dependent on burn-rate and, hence, in most studies, the variability caused by other effects within the same fuel type group has been overshadowed by factors such as stove type (Hartman and Rives 1985; Shelton and Gay, 1986). The study by Muhlbaier (1981) of emissions, from two softwoods and five hardwoods also confirmed this phenomenon. Typical particulate emission results (maintaining other variables of combustion as constant as possible) were:

•	softwoods	11.9 ± 2 g/kg
•	hardwoods	10.4 ± 2 g/kg

Surface Area

The log surface area is dependent on log size and geometry. Round logs with large diameter have the smallest surface area to mass ratio, in comparison with split logs and quartered logs. Emissions from residential wood combustion (RWC), therefore, also are influenced by log size and geometry. This effect has been explored by several researchers (Hubble et al., 1981; Cooke et al., 1982; Muhlbaier, 1981). Results indicated that particulate and organic emissions were considerably higher for the larger logs with smaller surface area to mass ratios (Muhlbaier, 1981).

However, CO emissions increased drastically with an increased surface area to mass ratio (Cooke and Allen, 1982) from 20 (lb/1000 lbs of wood) to 110 (lb/1000 lbs of wood) for surface area to mass ratios of 10 ft^2/ft^3 to 40 ft^2/ft^3, respectively.

Moisture Content

The moisture content of fuel wood has been known to influence the rate of combustion and the resultant emissions since man discovered fire. This factor of combustion has been studied extensively, and a good insight to the effects of moisture is presented in the following table (Weston, 1989). As evident in Table 1, particulate emissions increase significantly with increased moisture within the fuel wood. This effect is especially emphasized when values are normalized to the actual heat gained by the combustion process.

Operating Conditions

Operating conditions of the woodstove influence the combustion temperature and consequently the emissions generated. The study of the relationship between operating conditions and the resultant emissions is complicated by the stages of burning (burn cycle) (Hayden and Braaten, 1985), the stove type (Shelton and Gay, 1986), and the energy demand (heat required in relation to stove efficiency and rate of burning). The resultant physical factors produced by the above variables of combustion have been studied by numerous investigators and have been summarized in a concise diagram by Hubble et al., (1981) presented as Figure 1. The resultant emissions are highly dependent on these physical factors and these have been summarized for various stove types by Kowalczyk, Bosserman and Tombleson (1981).

Source Testing

The need for a standard source testing method was clearly recognized by the U.S. EPA and the standard EPA Methods 5G and 5H were developed for woodstove testing. While information exists for various airtight stoves, catalytic stoves, and the prototype wood pellet stoves, each stove type is unique in terms of characterization of emissions. Chemical characterizations of the RWC source generally have employed the specific test conditions of EPA modified Method V to identify the effect of factors such as wood type (e.g., oak or fir), and size of wood logs (6 inch diameter) with a common box type airtight stove (Rau, 1988).

Unfortunately, these test conditions do not reflect the actual conditions of RWC in Ontario. Firstly, the wood types used in the source characterization test performed to date are not in common use in Ontario. Oak is a comparatively expensive type of wood in Ontario and very little fir is grown because of local climate. Another variable that has not been addressed in the literature reviewed are emissions from Canadian manufactured woodstoves. Two very common types of woodstoves employed in Ontario are Kerr Titan and Fawcett WF 200.

Methods for source sampling of woodstoves for particulate emissions and organic compounds have been standardized (Cooke et al., 1984). The focus of the methodology is to quantify emissions from a specific stove type under rigorously defined conditions. The general methodology employs a standard type air-tight stove, with a sampling port that enables a sampling probe to collect a representative sample of the resultant mixture of flame gases and

TABLE 1

Impact of Moisture on Wood Net Heat Content and Particulate Emissions[1]

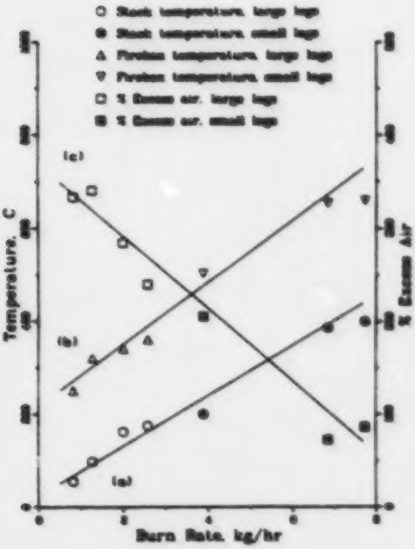
WOOD MOISTURE* CONTENT (%)	RELATIVE ENERGY CONTENT	RELATIVE PARTICULATE EMISSIONS PER POUND WOOD BURNED	RELATIVE PARTICULATE EMISSIONS PER NET BTU CONTENT OF WOOD BURNED
10%	1.00	1.0	1.00
20%	.88	1.2	1.36
30%	.67	1.5	2.25
40%	.59	1.9	3.22
50%	.47	2.4	5.10

* Wet basis, i.e., 10% moisture content = $\frac{\text{10 lb. water}}{\text{10 lb. water + 90 lb. wood}}$

[1] From Weston, 1989

FIGURE 1

Summary of Stack Temperature [curve (a)], Firebox temperature [curve (b)], and % Excess Air [curve (c)] versus Burn rate from Combustion of 0.12 -m- and 0.08 -m- Diameter Oak Logs.



suspended particulate matter (Allan et al., 1984). The following conditions have been standardized:

- wood species, size and shape (oak logs, 20 cm diameter);
- moisture content (20% W/W wet basis);
- minimum burn time;
- minimum sampling time;
- fuel charge weight (10 kg, dry);
- sample size (3 m^3 (STD, dry)); and
- steady-state operation.

While the purpose of standardizing these factors is to facilitate comparison between emissions from different stove types, these conditions do not reflect actual operating procedures and practices, local climate or local fuel wood types used.

The U.S. EPA emission factors discussed earlier are based on average values obtained through the standard testing procedure, conducted in various climatological locations. While these emission factors allow for an estimation of national emissions in the United States, their representativeness and applicability have been under review by the Inventory Management Division of Environment Canada. It was concluded that further work is required to quantify emission factors that reflect regional and temporal variability characteristics of Canadian Climates (Yandle, 1989) and wood fuels.

Residential Wood Combustion and Ambient Air Quality

A variety of objectives have motivated ambient air quality monitoring studies in areas with RWC impacts. One of the major objectives has been to determine the contribution of RWC emissions to ambient air quality - especially in regions with poor air quality (where existing ambient air quality standards are exceeded). Often, there are parallel studies for indoor monitoring to determine exposure of inhabitants while indoors, source characterization of emissions, as well as parallel surveys to determine wood consumption. Samples collected are analyzed for elemental species, ionic species, carbon analyses (C-14 isotopic composition, volatilizable (C_{vol}) and elemental carbon (C_{el})), a wide range of organic compounds - usually classified into polynuclear aromatic compounds (PAH), volatile organic compounds (VOC), as well as for the traditional pollutant gases (especially CO and NO_x). Recently, monitoring to determine the mutagenic activity of samples dominated by RWC emissions has been conducted.

Sampling Methods

Depending on the study objectives, sampling methods collect material for elemental (mainly inorganic), organic or biological data in three phases or modes:

1. particulate fraction;
2. gaseous fraction; and
3. combined particulate/gaseous fractions.

The sampling and to a lesser extent, analysis techniques that are used to determine ambient RWC impacts depend on the fraction required and hence, it is convenient to discuss methods for the collection of material in these phases.

Sampling of Particulate Phase Species

Sampling methods for ambient suspended particulate material commonly employ filter impaction of a known volume of air drawn through the filter matrix. Sampler types used include high volume samplers with or without size selection, and dichotomous samplers.

High volume samplers collect total suspended particulate matter, i.e., a full size range considered to contain particles of aerodynamic diameter 100 µm and less. Sampling rates are typically 1.13 to 1.70 m^3/min (40 to 60 ft^3/min). Samples generally are collected over a 24-hour period although some studies have used 12-hour (day/night sampling) sampling periods. Since particulate emissions from RWC appliances are predominantly in the 0.1 to 1.0 µm diameter size range (e.g., Kowalczyk and Greene, 1981), size selective sampling is often employed for ambient monitoring of RWC impacts. With the aid of a size selective inlet, high volume samplers collect suspended particles with a predetermined maximum cut-off diameter, typically 10 µm. When fitted with cascade impactors, high volume samplers collect particles in a number of particle diameter size ranges typically ~0.5 to 10 µm. Other samplers involving collection of particles on filter media, are in use and employ lower flow rates (low and medium volume samplers) with size selection of particles.

Dichotomous samplers have been the samplers that have been employed frequently in monitoring programs associated with the assessment of ambient RWC impacts. These samplers collect particles in two size ranges, usually < 2.5 µm (the fine or inhalable fraction) at (usually) 1.67 L/min, and 2.5 to 15 or 10 µm diameter - the coarse fraction at flow rates of (usually) 15 L/min. However, a limitation of low volume sampling is the possibility of filters plugging up in areas of heavy woodsmoke impact.

Sampling of Vapour Phase

The collection of vapour phase compounds is complicated by several factors:

- volatility;
- reactivity;
- break-through threshold; and
- stability of and consistency of sampling medium.

Gaseous compounds are not collected efficiently using filter paper impaction and adsorption; instead, actual volumes of air are collected, or alternatively, the vapour phase compounds are absorbed onto media that retain gaseous compounds with integrity over time. Sampling methods that have proven successful for gaseous compounds are:

- adsorbent tubes;
- tedlar bags;
- stainless steel canisters;
- direct cryogenic trapping; and
- impinger trains (generally used for source sampling).

Adsorbent tubes have been used extensively and the medium commonly used to adsorb low molecular weight hydrocarbons is activated charcoal. For a wider range of organic compounds, sorbent tubes are packed with tenax, carbosieve (molecular trap), fluorosil etc.; either exclusively or in combination. Since flow rate influences collection, and non-linearity and breakthrough occur in the high concentrations, the sampling protocol specifies up to four tubes be exposed in parallel. The quadruple sampling and analysis renders this method of sampling as costly, in comparison to Tedlar bags and canisters.

Combined Particulate and Gaseous Sampling

Several studies have been undertaken to determine the vapour particle distribution in Hi-Vol sampling (Cautreels and Van Cauwenberghe, 1977: Galasyn et al., 1984; Thrane and Mikalsen, 1981; Yamasaki et al., 1982; Davis et al., 1983; Dann et al., 1989) and also in low volume sampling (Bjorseth and Eklund, 1979; Andersen et al., 1988; Otson and Hung, 1983).

The distribution ratios of particulate to gas phase concentration of several PNA's as well as other classes of organics were reported by Cautreels and Van Cauwenberghe. For phenanthrene, anthracene, methylpyrene and methylanthracene, the distribution factors were 0.027 to 0.088; thus most of these compounds are in the gas phase. Fluoranthene, pyrene and benzofluorenes had intermediate values 0.26, 0.49 and 1.25 respectively while benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluranthene, benzo(a)pyrene, benzo(e)pyrene and perylene were primarily in the particle phase with distribution factors ranging from 3.14 to 11.5.

In some cases, more sensitive methods of analysis are desirable, such as neutron activation analysis (for elemental composition), and gas chromatography with mass spectroscopy (GC/MS), for organic and inorganic compounds.

Ambient concentrations are generally in the range of parts per billion (ppb) and thus, highly sensitive methods of analysis are required. Analytical methods commonly used to determine ambient concentrations include:

- gas chromatography (GC);
- gas chromatography with mass spectroscopy (GC/MS);
- ion chromatography (IC);
- high performance liquid chromatography with ultraviolet fluorescence (HPLC/UV-fluorescence);
- atomic absorption (AA);
- inductively coupled plasma (ICAP);
- thermal optical reflectance (TOR);
- neutron activation analysis; and
- X-ray fluorescence.

Studies to evaluate the impact of emissions from residential wood combustion initially examined the particulate emissions in the fine size fraction (0.01 to 1.0 μm) since source testing information indicated that most (> 90%) of the particulate emissions from RWC were in the fine fraction (Muhlbaier, 1982). Airshed studies focused on upwind/downwind mass loadings in the fine fraction. This was frequently accompanied by questionnaires addressing burning practices of the homes sampled. The need for better source resolution is evident, since all combustion sources display similar particle size distributions. Subsequent studies have followed the following designs:

a) upwind/downwind with particle sizing and chemical analysis;
b) outdoor sampling with source apportionment (using inorganic and organic woodsmoke characterizations); and
c) tracer studies.

Impact Studies in the United States

During the late 1970's and 1980's the rise in interest in RWC and the accompanying environmental concerns prompted air monitoring studies in several areas of suspected impact. Issues of non-attainment of aerosol and CO objectives prompted federal action to investigate the effects of residential wood combustion in various US EPA programs.

The major pre-1985 U.S. studies have been reviewed with respect to strategy and methodology employed in an EPA study (Hartman and Rives, 1985). Ambient data from the major RWC studies were compiled in a Technical Support Document (EPA-450/4-85-012). The ambient air quality data were summarized with references as part of this study. Average RWC impact determined in these studies were estimated for the fine mass fraction. The percentage contribution of RWC to the fine fraction ranged from 1.5% to 72.8%. Average ambient concentrations of carbon monoxide ranged between <1 ppm to 2.7 ppm (8 hour average). Of major concern in RWC studies, has been the incremental burden of benzo(a)pyrene (BaP) caused by woodsmoke emissions. Ambient BaP levels in one U.S. location was found to be above 100 ng/m^3.

The physical and chemical characteristics of emissions caused by most combustion processes are so similar that this grouping of sources is extremely difficult to separate. The overlapping nature of temporal and spatial distributions of sources, such as residential wood combustion and automotive emissions, also augment these difficulties.

An average source profile for residential woodstoves has been compiled by several investigators in the following locations: Medford, Oregon, Portland/Seattle and Pocatello, Idaho. These profiles have been provided by J. Core and are included in Figure 2, however, the aforementioned conditions and limitations restrict the usefulness and applicability of these profiles.

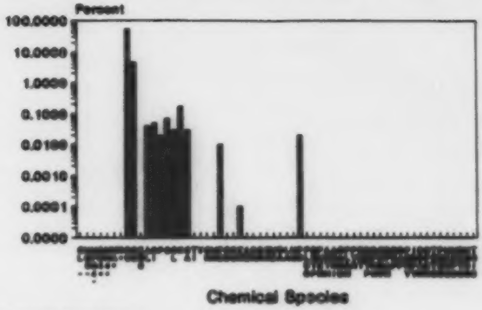
A variety of methods, and combinations of such, have been used to resolve woodsmoke emissions from other sources. The objective of assessing relative source contributions can be categorized into two domains:

i) statistical methods; and
ii) direct identification methods.

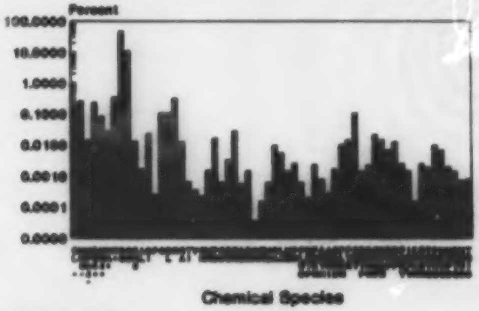
Statistical methods have evolved from hypothesis testing, multivariate regression techniques, factor analysis and matrix reductions. Mathematical models also have been developed to simulate indoor and outdoor dispersion of source emissions. Specifically, the methods of source apportionment that are statistical in nature comprise:

- hypothesis testing (e.g., upwind/downwind comparisons);
- regression techniques (least-squares, linear, curvilinear and multivariate);
- factor analysis (an extension of the multivariate regression techniques employing matrix manipulations);
- chemical (or elemental) mass balance (simultaneous solving of linear mass balance equations); and
- mathematical simulation equations (dispersion modelling).

FIGURE 2


Woodstove Source Profile
PM-2.5 Fraction (JA Rau Thesis)

Pacific NW Profile Project


Woodstove Source Profile
PM-2.5 Fraction Composite

Pacific NW Profile Project

Statistical methods have evolved from single variable regression to more sophisticated methods such as CMB analysis and mathematical simulation (modelling) for numerous environmental concerns. Whether the source is simple or complex; if the emissions from a process or reaction are easily identified with accuracy and reproducibility, these sources can be resolved with an average characterization of the source. The variabilities that impinge upon wood burning emissions characterizations, represent new challenges in source apportionment techniques. The direct methods of RWC emissions identification, probe for direct evidence of the source's influence on ambient samples. Two common methods of identification are:

- morphological investigation; and
- source tracing via tracer compound(s) or other source characteristic(s).

Conclusion

This review has cited studies of several areas in the U.S. and Canada in which there have been adverse air quality impacts. The climate of most areas is similar to that in Ontario - in the sense of winter temperatures; and for several areas that are located in mountainous areas and with orographic features (valleys, bowl shaped topography) conducive to poor dispersion conditions. However, the potential for adverse RWC air quality impacts are largely dependent on the extent of RWC use. In areas where there is heavy use of residential wood fuel, the potential will therefore exist. In order to assess the potential impacts, the obvious action is to conduct specific monitoring activities to assess the extent of the impacts. Methods for conducting such assessments, and factors that should be addressed in such a study have been reviewed. These factors specify the scope of the required study. In particular, the assessment could involve ambient air monitoring and analysis tracer methodology (e.g., potassium), and source characterization and data analysis, such as receptor modelling (Chemical Mass Balance (CMB)).

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A11

A STUDY OF THE PEAK OZONE LEVELS IN THE TORONTO AREA

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BACKGROUND

The concentration of ozone in the Toronto area exceeds Ontario's regulatory limit more often than any other pollutant. During the year Ontario's Air Quality Index was first introduced, (June 1988 to May 1989), Shenfeld and Yap (1989) reported that between 80 and 95% of the hours that the Air Quality Index was in the Moderate to Poor range within Metropolitan Toronto, ozone was the major pollutant. Furthermore, during the summer of 1988, the ozone hourly averages were frequently well above 120 ppb, (AQI=50), which is known to cause an impact on health to a large percentage of the population, especially those who may be exercising outdoors. These high ozone developments occurred during periods of long-range transport (LRT) of ozone and precursors into the Province from United States. During the summer of 1989, the occurrences of high ozone readings were much less frequent, as the LRT conditions were not as prevalent, even during ozone conducive weather such as warm, sunny and relatively windless conditions.

Kurtz et al. (1989) have utilized the long-range transport Acid Deposition and Oxidant Model (A.D.O.M) to show the influence of U.S. emissions of nitrogen oxides and reactive hydrocarbons to the levels of ozone in Southern Ontario. Air mass back trajectory studies, most recently by Yap et al. (1988) established that U.S. sources of these pollutants were responsible for much of the high ozone values reported in Southern Ontario.

Ozone studies by Shenfeld (1977), Mukammel et al. (1982), and more recently Yap et al. (1988), established the meteorological conditions required for the development of high ozone levels in Southern Ontario. Studies of ozone developments in other geographical locations by Hewlett (1978), Wolff and Lioy (1978), Prior et al. (1981), Simpson et al. (1983), and Robeson and Steyn (1990) have established that peak hourly average levels of ozone can be correlated to specific meteorological parameters.

STUDY OBJECTIVES

The main objective of this study is to determine the proportion of the peak ozone levels in Toronto resulting from the LRT of precursors and ozone into Toronto. A second objective is to determine whether the relationship between peak ozone levels and meteorological parameters can be used to predict the peak ozone levels and hence the Air Quality Index for the afternoon and early evening. The third objective is to determine the relationship between the peak hour ozone level and the maximum 8-hour average the same day and what the 8-hour averages are with peak hour levels of 80 ppb (moderate air quality) and 120 ppb (poor air quality).

STUDY DESCRIPTION

For this study, we have selected the peak hour ozone levels during each day from May to September inclusive, for the years 1988 and 1989, during which the Pearson International Airport reported temperatures equal to or exceeding 23°C and the cloud cover was equal or less than four tenths opacity. The selected days were then separated into days that LRT occurred from the industrial States and those that it did not. This classification was determined by using synoptic weather maps and the Ontario Ministry of the Environment Air Resources Branch archives of the back trajectories of air into Toronto.

Three Metropolitan Toronto ozone recording locations were selected for study, namely; Downtown Toronto (Breadalbane), Scarborough (Lawrence and Kennedy) and North York (Yonge and Finch).

For LRT and non-LRT days, multiple regression equations are used to relate the peak ozone levels at each of the above locations with the Pearson International Airport maximum temperature, average wind speed and average cloud cover during the hours of 9AM to 4PM. Another dependent variable used, is the peak hour ozone level measured the previous day at the rural station outside Simcoe, Ontario. The difference between the peak ozone levels determined from equations with LRT and with non-LRT is used to determine the contribution of ozone to the Metropolitan Toronto locations due to LRT.

REGRESSION ANALYSIS

A multiple regression analysis was completed for the three sites (Toronto, Scarborough and North York) for each of LRT and non-LRT days. A simple regression equation was derived from the ozone data set of the Ontario Ministry of the Environment:

$$Y = B_0 + B_1 * X_1 + B_2 * X_2 + B_3 * X_3 + B_4 * X_4 \qquad (1)$$

where: Y - Maximum Ozone Level (PPM)
X_1 - Maximum Temperature (°C)
X_2 - Average Wind Speed (Km/hr)
X_3 - Average Cloud Opacity (10^{ths})
X_4 - Previous Day's Maximum Ozone (PPM)
Recorded at Simcoe, Ontario

The results of the regression analysis are outlined in Table 1.

The overall significance of the multiple regression can be tested by an analysis of variance. This test is equivalent to testing the null hypothesis that in the population from which the observations have been sampled, there is no significant regression of the dependent on the independent variables. The test consists of determining the F ratio for each case, that is the ratio of the mean square of the sum of squares of the regression over the mean square of the sum of squares of the residual. If the computed F exceeds the tabled value for a selected level of confidence, then the null hypothesis is rejected.

The F ratio is found at the bottom of Table 1. In all cases, the null hypothesis can be rejected at 5% level of confidence.

The effect of LRT from the industrial United States can be determined, at any particular site, from the difference in the predicted ozone levels using identical values for the independent variables in both the LRT and non-LRT regression equations. This difference was determined by using the above equations and all combinations of: air temperature being equal to 23, 27, 30 and 34 degrees C, wind equal to 0, 5, 10 and 20 km/hr., cloud cover equal to 0, 2, and 4 tenths, and the previous day's ozone equal to 40, 60, 80, 100 and 120 ppb. The results showed a minimum increase due to LRT to be 24.2% (13.7 ppb), a maximum increase of 48.7% (38.1 ppb) and an average of 31.7% (25.9 ppb). However, it can be expected that the effect of LRT to increase ozone concentrations would be even greater than indicated in this analysis which does not take into account the difference in means. The mean of the previous day's ozone is 15 ppb larger during LRT than non-LRT days (see Table 1) and all of the regression equations are positively correlated with the previous day's ozone.

TABLE 1 : MULTIPLE REGRESSION EQUATIONS
MAXIMUM OZONE LEVEL PREDICTION
(MAY 1988 to SEPTEMBER 1989)

	TORONTO [LRT]	TORONTO	SCARBOROUGH [LRT]	SCARBOROUGH	NORTH YORK [LRT]	NORTH YORK
N	35	41	36	42	30	35
B_0	-71.798	-54.829	-59.189	-23.973	-66.524	-27.924
B_1	5.166	3.931	4.985	3.333	5.335	3.301
B_2	-1.026	-0.894	-1.330	-1.008	-1.047	-0.949
B_3	-0.524	-1.625	-0.679	-2.525	-1.902	-1.413
B_4	0.152	0.115	0.125	0.099	0.109	0.051
R	0.805	0.679	0.698	0.653	0.685	0.696
R^2	0.648	0.461	0.487	0.427	0.470	0.485
SE	15.410	19.777	17.515	19.556	21.621	12.941
Y	72.818	55.133	76.111	56.000	77.268	57.241
X_1	29.230	26.300	29.229	26.350	29.461	26.938
X_2	14.153	13.128	13.952	12.806	14.231	15.257
X_3	1.923	1.895	1.880	1.862	2.177	1.801
X_4	72.659	55.967	72.756	56.563	74.146	57.931
F	14.375*	6.279*	8.653*	6.088*	10.161*	6.622*

N - Number of Observations
B_0 - Multiple Regression Coefficient (intercept)
B_1 - Multiple Regression Coefficient (for X_1)
B_2 - Multiple Regression Coefficient (for X_2)
B_3 - Multiple Regression Coefficient (for X_3)
B_4 - Multiple Regression Coefficient (for X_4)
R - Correlation Coefficient
R^2 - R-Squared
SE - Standard Error of the Estimate (PPB)
Y - Mean Measured Ozone (PPB)
X_1 - Mean Maximum Temperature (C)
X_2 - Mean Average Wind Speed (Km/hr)
X_3 - Mean Average Cloud Opacity
X_4 - Mean Previous Day's
Measured Ozone at Simcoe (PPB)
F - F - Ratio

Significant at the 5% Level of Confidence

MODEL TEST

The multiple regression equation, as a predictor of peak level ozone, was tested by using independent data sets from May to September 1987 for the Toronto and Scarborough sites. Measured peak ozone levels were compared against predicted peak ozone levels by using the appropriate regression equation, the relevant meteorology and the measured previous day's ozone at Simcoe. Figure 1 shows the graph of the total measured versus. predicted ozone levels for all study locations.

Willmott (1982), citing several examples showing that real significance and statistical significance do not exhibit a close correspondence, has proposed measures of 'systematic' and 'unsystematic' error to examine the types of differences and an 'index of agreement' to investigate the relative size of differences. Because a model should explain most of the major trends present in the observed record, it is important to know what proportion of RMSE is systematic ($RMSE_s$) and what proportion is unsystematic ($RMSE_u$). In this fashion, with respect to a 'good' model, $(RMSE_s)^2$ should approach zero while $(RMSE_u)^2$ should approach RMSE. The 'index of agreement' (D) was proposed to yield a measure of the relative size of differences; this index is intended to be a descriptive measure which is both relative and bounded ($0 \leq D \leq 1$) and can be widely applied in order to make cross-comparisons between models. As the agreement between the observed and predicted variables increases, D approaches 1.0 .

Table 2 contains the model performance statistics. It should first be noted that the calculated and measured population means and standard deviations are very similar, in fact in no case is the difference between the two means greater than 2 ppb.

The MAE and RMSE indicate a mean difference between the predicated and observed values of approximately 13 ppb. With the unsystematic portion of the RMSE being around 10 ppb, this indicates that most of the RMSE is unsystematic and it need not be assumed that there is a missing independent variable in the regression analysis.

The last column of Table 2 contains the model performance statistics for the combined "computed versus. measured" matrix. This is included to increase the size of the population to be 'large' ($N>30$) since the general utility of such indices as RMSE is questionable as N becomes small (Willmott, 1982). The high value of the Willmott Index of Agreement (D) (0.853) indicates a reasonably good agreement between the predicted and measured peak ozone levels.

FIGURE 1 : OBSERVED VS PREDICTED MAXIMUM OZONE LEVELS
TOTAL FOR 1987

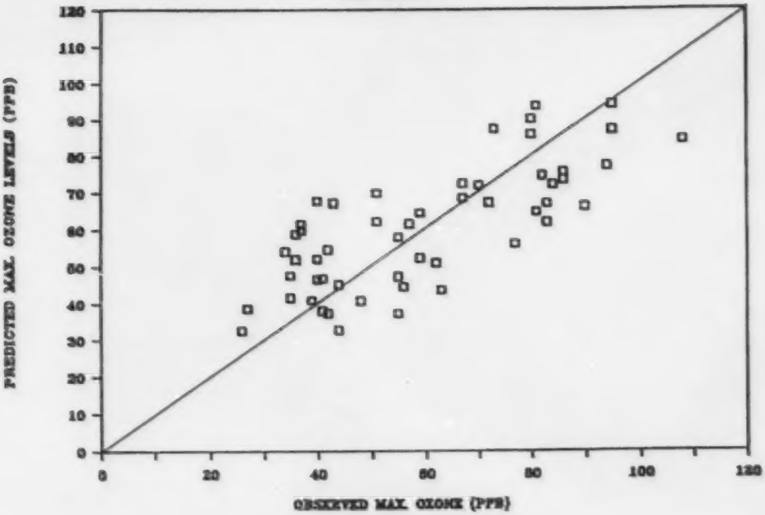

TABLE 2 : OZONE LEVEL PREDICTION
MODEL PERFORMANCE STATISTICS

	TORONTO [LRT]	TORONTO	SCARBOROUGH [LRT]	SCARBOROUGH	TOTAL	
N	12	16	11	15	54	- Number of Observations
O	69.000	48.312	73.273	55.866	60.092	- Average Observed Ozone
P	69.112	50.291	74.064	56.517	61.033	- Average Predicted Ozone
So	19.621	17.647	22.865	17.410	21.190	- Observed Standard Deviation
Sp	17.163	12.424	18.714	10.907	16.915	- Predicted Standard Deviation
a	0.693	0.526	0.470	0.432	0.684	- Slope of Regression Line (OBS vs PRED)
b	27.512	24.757	39.547	32.953	24.733	- Intercept of Regression Line
MBE	0.112	1.978	0.731	0.650	0.940	- Mean Bias Error
MAE	11.672	10.557	15.256	10.536	11.866	- Mean Absolute Error
RMSE	13.928	12.490	16.816	12.479	13.784	- Root Mean Square Error
RMSEs	7.527	8.295	11.572	9.747	8.376	- Systematic Portion of RMSE
RMSEu	11.713	9.348	12.201	7.781	10.959	- Unsystematic Portion of RMSE
r^2	0.486	0.483	0.413	0.483	0.373	- R-Squared
D	0.821	0.816	0.764	0.763	0.853	- Wilmott Index of Agreement

8-HOUR AVERAGE OZONE LEVELS

The final part of this study deals with the relationship between the peak hourly ozone level and the 8-hour average on the same day. The data set used for the determination of the regression equations is used here to determine the linear regression between the observed peak ozone (Y) and the 8-hour average (X_o) by the equation:

$$Y = B_o + B_1 * X_1 \tag{2}$$

Table 3 shows the linear regression equation for each site and for each of LRT and non-LRT days. From the table we can see a high level of correlation with an average correlation coefficient (R) of 0.95 and an average coefficient of determination (R^2) of 0.89 . Using these linear equations it is possible to estimate the 8-hour average associated with a peak hourly ozone level of 80 ppb (moderate air quality) and 120 ppb (poor air quality). These values are listed on Table 3 and are equal to, on average, 62 and 91 ppb, respectively. Figure 2 shows graphically the total relationship between peak hourly ozone and the 8-hour average ozone for all study locations.

SUMMARY AND CONCLUSIONS

This study has determined that the level of ozone in Metropolitan Toronto increases on LRT days. These increases in ozone averaged approximately 32% (26 ppb) and peaks as high as 49% (38 ppb) were noted. These results are compared with Wolff and Lioy (1978), who concluded by a similar means that the contribution of external sources to a Connecticut location during high ozone days, was as much as 75 ppb, and Prior et al. (1981) reported the LRT contribution to St. Louis was 36 ppb.

Multiple regression equations were determined relating the peak hour ozone levels with the same day maximum temperature, the average daytime windspeed and the cloud opacity at Pearson International Airport and the peak hour ozone concentration at the Simcoe rural station for the previous day, for LRT and non-LRT days in 1988 and 1989. Data for 1987 were used to validate the statistically determined relationships. These equations have proven to be reasonabley good predictors of peak ozone levels in the Metropolitan Toronto area.

[illegible]

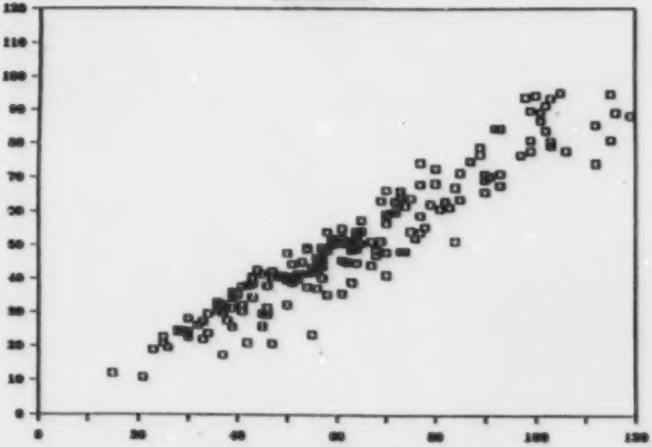

TABLE 3 : [illegible]

[illegible]

	[illegible] ([illegible])	[illegible]	[illegible] ([illegible])	[illegible]	[illegible] ([illegible])	[illegible]	
N	39	41	39	42	30	30	- Number of Observations
Bo	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Linear Regression Coefficient (Intercept)
B1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Linear Regression Coefficient (for X)
R	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Correlation Coefficient
R^2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- R-Squared
SE	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Standard Error of the Estimate (PPB)
Y	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Mean 8 Hour Average Ozone (PPB)
X	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Mean Peak Hourly Ozone (X)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Value of 8 Hour Average Calculated for a Peak Ozone Level of [illegible] PPB
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	- Value of 8 Hour Average Calculated for a Peak Ozone Level of [illegible] PPB

The study also indicated that Ontario's 80 ppb one-hour average regulatory limit cannot be used as a surrogate for an eight-hour average health standard. The World Health Organization Guidelines recommend 50 to 60 ppb for an eight-hour average level of ozone for the protection of human health.

Similar studies could be carried out in the future to determine regression equations for peak hourly ozone for other cities of Southern Ontario, for both LRT and non-LRT days. The regression equations can be used to predict the peak ozone levels and the associated AQI for each location.

ACKNOWLEDGEMENTS

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A12

DEVELOPMENTS OF MONITORING METHODS FOR ODOROUS ORGANICS IN AMBIENT AIR

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INTRODUCTION

Odour nuisances have been reported in connection with facilities such as water treatment plants, kraft mills, rendering plants and oil refineries. The problem is that often the odour detection limit for the airborne compounds are lower than the current analytical detection limits: this is true particularly with sulfur containing compounds.

In the present study we have evaluated recent methods for the detection of four classes of compounds associated with odour complaints: aliphate amines; carbonyl compounds; short chain fatty acids; and sulfur containing compounds. With the exception of certain target sulfur compounds (for which we use thermal desorption/GC/MS)[1], the process of chemical derivatization followed by HPLC using either U.V. or fluorescent detection appears to be the best approach for obtaining detection limits in the low parts per billion range for most compounds under study.

METHODS

I AMINE ANALYSIS

SAMPLE PREPARATION[2]

Sep-PAK C_{18} cartridges were purchased from Waters Scientific, Mississauga and prepared as described below.

The Sep-PAK is initially washed with 5 mL methanol by attaching a syringe full of the solvent to the luer-look end of the cartridge and slowly passing methanol through. A second wash is then performed with a 3% (V/V) phosphoric acid solution in methanol using the same technique as above. The two ends of the Sep-PAK are then touched to a kimwipe, in order to remove any excess liquids.

The Sep-PAK is then placed in a vacuum manifold (Supelco Canada Inc.) and dried for one hour under reduced pressure and a nitrogen stream. Following this, the cartridge is placed directly under a stream of nitrogen for one half hour and a flow-rate of 80-100 mL/minute. The Sep-PAKS are placed in individually capped and labelled glass vials, and stored in a cool, dark, dry place for up to four weeks.

SAMPLING

Ambient air is drawn through the Sep-Pak cartridge at a known rate. The rate of pumping is measured before and after sampling

ANALYTICAL PROCESSING AND DERIVATIZATION

A stock basic methanol solution is prepared by weighing 0.166 g of KOH (BDH, Toronto) and dissolving it in 100 mL of distilled-in-glass methanol (Caledon, Georgetown). The derivatizing solution is made up by dissolving 0.200 g of 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl)(Aldrich) in 100 mL of the above basic methanol solution.

A 1 mL aliquot of NBD-Cl solution is then pipatted into 10 mL capped and labelled centrifuge tubes. Into these tubes the trapped amines are eluted by passing 5 mL of potassium hydroxide/methanol stock solution through the Sep-PAK cartridge. The tube is capped, vortexed for several seconds and incubated for a minimum of 24 hours at room temperature.

ANALYTICAL SYSTEM AND CONDITIONS

A Hewlett Packard model HP1090 HPLC system with the following components is used:

- gradient solvent delivery system
- variable volume injection system with autosampler
- variable wavelength, programmable fluorescence detector
- integrator with a data system
- heated column compartment

The column necessary for the separation of the amines is Supelco's Supelcosil LC-18-S, a base deactivated, reversed phase octadecylsilane column. The column dimensions are: 25 cm x 46 mm with a 5 um particle size. The chromatographic conditions are listed below.

SOLVENT DELIVERY

Initial:	45% methanol, 55% water
6 minutes:	60% methanol, 40% water
Run time:	15 minutes
Flow rate:	1.5 mL/minute
Column Oven Temp:	40°C
Injection Volume:	20 uL

DETECTION

Lambda Excitation:	470 nm
Lambda Emission:	530 nm
Photomultiplier Tube Gain:	18 (maximum)
Response Time:	1000 msec

II ALDEHYDES AND KETONES ANALYSIS:

DNPH SOLUTION FOR COATING SEP-PAKS [3]

20.0 ml of saturated DNPH solution are added to 200 ml acetonitrile in a 1L volumetric flask with glass stopper. 1.0 ml conc H_3PO_4 is added, and solution shaken and made up to 1L volume with acetonitrile. The purity level of the solution is checked using HPLC.

COATING OF SEP-PAK CARTRIDGES

Each Sep-Pak is flushed with 10.0 ml acetonitrile using 10-ml syringe. An 7.0 ml aliquot of DNPH solution is dispensed through the Sep-Pak at a rate of 2.0 ml/min.

U.H.P. grade nitrogen is blown through the Sep-Paks via a DNPH guard column and drying manifold. (The use of paper towels should be avoided as these contain formaldehyde), at the rate of 50-100 ml/min for a few minutes (until no excess solvent droplets appear. Cartridges are then plugged at each end with luer lock male plugs and stored individually in glass culture tubes with either Teflon or polypropylene caps (Bakelite caps should be avoided as they are a source of formaldehyde)

PREPARATION OF DNPH-CARBONYL STANDARDS [4]

FORMALDEHYDE, ACETALDEHYDE, PROPIONALDEHYDE, ACETONE

A saturated solution of DNPH in 2N HCl is titrated with each of the above carbonyl compounds. The colored precipitate is washed with 2N HCl and water and air dried. Purity of derivative is determined by HPLC.

ACROLEIN, BUTYRALDEHYDE, BENZALDEHYDE, GLUTYRALDEHYDE [5], CYCLOHEXANONE (INT. STD).

The DNPH derivatives of these compounds are prepared by adding the carbonyl compound dropwise to an acidic solution of DNPH in dimethylsulfoxide (DMSO). The colored precipitate is filtered and washed with 2N HCl, and water. Purity is checked by HPLC. Individual stock solutions are prepared by dissolving 10 mg. of solid derivative in 100 ml of acetonitrile. A stock mixture of derivatives is similarly prepared.

ANALYTICAL PROCESSING

Sep-Paks are eluted with 3.0 ml acetonitrile using a 5.0 ml syringe giving a final volume of 2.8 ml of eluent.

Samples are run on Hewlett Packard HPLC 1090A system using the following equipment and conditions (Figure 2).

Phenomenex 150 mm x 4.6 mm. ODS C_{18} column (or equivalent).

Hewlett Packard Diode array detector (or equivalent)

Solvent: 60% acetonitrile, 40% water.
Flow 1.0 ml/minute
Analytical wavelength 360 nm.
Oven temp. $40^{\circ}C$

GLUTYRALDEHYDE (1.5-PENTANEDIAL)

The following analytical conditions are used to chromatograph the DNPH derivative of glutyraldehyde.

Column: Zorbax CN column 4.6mm x 150mm
Mobile Phase
55% acetonitrile / 45% H_2O / 0.1% H_3PO_4

III CARBOXYLIC ACID ANALYSIS

PREPARATION OF STANDARDS

1-Pyrenyl diazomethane (PDAM). 50 mg of 1-pyrenecarboxaldehyde is suspended in 3 ml DMSO ; 0.3 ml of hydrazine monohydrate is added with stirring, and the mixture stirred at 50-$60^{\circ}C$ for 3 hours. The yellow crytals of 1-pyrenecarboxaldehyde hydrazone are filtered and recrystallized from ethanol. Purity is checked by HPLC.

To 20 mg of the hydrazone suspended in 5 ml of diethyl ether and added 65 mg of activated manganese dioxide and the resulting mixture allowed to react in an ultrasonic water bath for 90 minutes. The manganese dioxide is filtered and the reddish-orange filtrate evaporated to dryness under nitrogen yielding red crystalline PDAM.

DERIVATIZATION OF FATTY ACIDS

To 2 mg of acid in 2.0 ml methanol are added 2.0 ml of 0.4% w/v solution of PDAM in ethyl acetate. The mixture is stirred for 2 hours at room temperature after which time a single peak is obtained on the chromatogram.

SEP-PAK PREPARATION

C18 cartridges are loaded with 1% sodium hydroxide in methanol. The cartridges are dried by flushing with pure nitrogen.

Recovery studies using standard fatty acids loaded onto prepared Sep-Paks, elution, and subsequent derivatization indicate recoveries >80%.

ANALYTICAL PROCESSING

HP1090 system with fluorescent detection (lamda $_{ex}$ 340nm, lamda $_{em}$ 397nm)

Column: 15 cm Merck lichrosphere ODS (5u)
Solvent: 70% acetonitrile/30% water

STANDARD GAS GENERATION

Gas standards for individual target compounds are generated using a VICI Metronics dynacalibrator system, equipped with internal pump. Generated gas standards are diluted with zero air to give final concentrations in the low ppb range.

QA/QC

For samples a 20% QA/QC program should be implemented. This calls for 10% duplicate samples, 5% blanks and 5% spike recoveries.

RESULTS AND DISCUSSION

CHROMATOGRAPHY OF DERIVATIZED AMINES, CARBONYLS AND CARBOXYLIC ACIDS

Recoveries at three levels for target amines and carbonyl compounds are generally better than 85%. Preliminary studies on the carboxylic acids indicate similar recoveries.

Detection limits for target amine and carbonyl compounds are given in Tables 1 and 2. These detection limits correspond to a signal to noise ratio 5:1 and are determined by sequential dilution of stock standards. The ppbv values are based on an air sample of 150 litres for amines, and 100 litres for carbonyls.

CARBOXYLIC ACIDS AND SULFUR COMPOUNDS

Detection limits for target carboxylic acids are given in Table 3. It is clear that the derivatization of carboxylic acids using the fluorescent tag pyrenyl diazomethane (PDAM) provides a sensitive means of determining this class of compounds.

With the exception of butyric and isobutyric acid, which co-elute, good chromatographic separation is obtained for the remaining target compounds and recoveries from the C18 Sep-Pak are good (>80%).

The group of sulfur compounds owing to their reactivity, instability and low odour thresholds pose the greatest challenge. The thiols are amenable to derivatization using 7-Chloro-2, 1,3--benzoxadiazole-4-sulfonate (SBD-Cl)[7] with subsequent HPLC determination using fluorescent detection. Recent studies indicate that a structurally similar fluorescent tag may be used to derivatize disulfides[7,8]. We are presently investigating this in conjunction with a thermal desorption GC/MS method.

CONCLUSIONS

With the possible exception of sulfur compounds (methods for which are currently being evaluated) the process of concentrating airborne odorous compounds on to a suitable matrix, with either in-situ or post elution derivatization followed by HPLC, allows detection limits in the low ppbv range to be attained. Whilst the procedures are not new, the optimisation of variables (such as cartridge packing material, flow rates through the cartridge, pH of eluting solvent) combined with the development of a sampling train for field us for all four compound classes will provide the unique capability of narrowing the source of an odour problem to a compound group with subsequent quantitation.

TABLE 1

Method Detection Limits for the Analysis of Aliphatic Amines in Air

	Method Detection Limit (ppb)	RDS (%)	Degree of Error "D" (ppb)	Lower Limit (ppb)	Upper Limit (ppb)
Methylamine	0.105	6.36	0.011	0.093	0.117
Dimethylamine	0.043	4.99	0.001	0.041	0.044
Ethylamine	0.063	10.5	0.006	0.056	0.069
n-Propylamine	0.039	15.3	0.005	0.034	0.045
Diethylamine	0.809	13.6	0.129	0.68	0.938
n-Butylamine	0.040	5.1	0.001	0.039	0.042

TABLE 2

Method Detection Limits for Carbonyl Compounds

	Detn Limit ng for 20 ul inj.	*Detn Limit ppb_v	RSD %	Degree of Error "D"	Lower Limit ppb_v	Upper Limi t ppb_v
Formaldehyde	1.00	0.14	10.71	0.014	0.13	0.15
Acetaldehyde	0.90	0.13	18.45	0.022	0.11	0.15
Propionaldehyde	1.98	0.20	13.20	0.026	0.17	0.23
Butyraldehyde	2.30	0.25	24.80	0.058	0.19	0.31
Benzaldehyde	3.20	0.39	7.63	0.028	0.36	0.42
Glutyraldehyde	2.00	0.15	17.30	0.025	0.13	0.18
Acrolein	3.50	0.30	12.00	0.034	0.27	0.33
Acetone	3.00	0.25	16.40	0.039	0.21	0.29

* Based on a 100 litre air volume.

TABLE 3

Method Detection Limits for Fatty Acids*

	Detection Limit Femtomoles for 20 ul inj.	Detection Limit (ppt_v)	RSD (%)
Acetic Acid	100	6.0	12.5
Propionic Acid	200	12.0	13.9
Isobutyric/	300	18.0	14.6
Butyric Acid	200	12.0	10.8
Isovaleric Acid			
Valeric Acid	200	12.0	15.1

* Signal to noise ratio 5:1
ppt_v based on 100 litre air volume

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ATMOSPHERIC MEASUREMENTS OF NATURAL HYDROCARBONS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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BACKGROUND

This OME-sponsored project was initiated in 1988, as part of the Eulerian Model Evaluation Field Study (EMEFS), to obtain data on atmospheric concentrations of a number of key volatile organic compounds (VOC), particularly biogenic hydrocarbons such as isoprene and mono-terpenes. These data are needed for an assessment of the relative importance of NO_x and VOCs, and natural vs. anthropogenic VOCs in the oxidant and acid rain problems. Notably, international, national and provincial decisions on control strategies for oxidant precursors are at present in various stages of formulation. For example, the Federal/Provincial LRTRAP (Long Range Transport of Air Pollutants) Committee is developing a management plan for dealing with Canada's O_3 problem and meeting Canada's international obligations under the NO_x/VOC protocol [1]. There remain numerous outstanding scientific issues concerning the formation of O_3 and other oxidants. To review ongoing oxidant-related research in Canada and to identify the knowledge gaps to be addressed in the future, an National Oxidant Research Workshop was held recently under the auspices of CIRAC (Canadian Institute for Research in Atmospheric Chemistry) [2]. It was concluded at that workshop that there exists a critical lack of data on the temporal and spatial distributions of natural VOCs as well as their sources and emission rates in representative Canadian settings.

Scope of this project encompasses (1) the development of GC and GC/MS-based analysis of ambient C_2-C_{10} hydrocarbons; (2) measurements of these hydrocarbons at the Ministry's site at Dorset and other forested areas; and (3) statistical analysis and chemical modeling of the data thus obtained, in collaboration with other CIRAC scientists. While substantial progress is being made on all these research areas, this report will focus on the results of the analysis of the 1988 Summer EMEFS data to illustrate the current knowledge on the relative importance of natural and anthropogenic hydrocarbons in oxidant formation in Eastern North American rural atmospheres and on the meteorological factors controlling the atmospheric concentrations of isoprene, the dominant natural VOC emitted by deciduous trees. This Canada-US joint study represents the most extensive measurements of nonmethane hydrocarbons (NMHCs) carried out to date on a regional scale during summer months when multi-day O_3 episodes occur frequently. The PI has been requested by the participants to carry out site-to-site comparisons of these data to discern site-specific and regional features. Presented in this paper is a brief summary of these data analyses.

(I) 1988 Summer EMEFS Data on Hydrocarbons

Comprehensive measurements of speciated NMHCs were made concurrently during July and August in 1988 at four rural sites in eastern North America (i.e. Brasstown Bald, Georgia;

Dorset and Egbert, Ontario; and Scotia, Pennsylvania). These NMHC measurements were carried out together with other key atmospheric species as part of the enhanced ground site measurements of the EMEFS (Eulerian Model Evaluation Field Study) program [3]. The participants in the NMHC measurement program were groups from Georgia Tech. (Brasstown Bald); NOAA and U. of Washington (Scotia); and AES, OME, C & P, Hydro, Concord Scientific and York U. (Canadian sites). The data from Dorset and Egbert have been archived in an AES report [4].

A summary of the NMHC data obtained at the four rural sites are presented in Table 1. The NMHC compounds listed in these tables are representative of both natural and anthropogenic species but do not include all the identified species containing up to C_{10}. Namely, by class, the C_2-C_{10} hydrocarbons listed are: (1) alkyne and alkene (acetylene, ethylene and propylene); (2) alkane (ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, 2-methyl pentane, 3-methyl pentane, n-hexane, n-heptane and n-octane); (3) aromatic (benzene, toluene, o-, p- and m-xylenes and ethylbenzene); and natural NMHCs (isoprene, α- and β-pinene). α- and β-pinene were not measured by the Canadian group. The median concentrations indicated in this table are based on the data obtained between 8:00 to 17:00 EST. Night-time data were not included in these analyses because they are susceptible to influence of nocturnal inversion layer and also because natural NMHC isoprene emission presumably occurs only during the daytime [5]. The spread of the data is also shown in this table in terms of the data ranges of ±67 %. Inspection of the frequency distributions indicated that all the NMHC data are significantly skewed. Therefore, for the purpose of making site-to-site comparisons of these data, median values are judged to be more meaningful than mean values, and thus are used throughout the discussions presented below. For ease of visual inspection, concentrations of individual NMHC species at the four rural sites are shown graphically in Figures 1-4, for the four NMHC groups described above, i.e. alkyne and alkene, alkane, aromatic and natural compounds. Notable features of these site-to-site comparisons are annotated below.

Alkyne and Alkene (Fig.1): The data range for each of these hydrocarbons overlaps to a great extent from site to site. However, the median values plotted in this figure do exhibit an apparent trend of being lower at Brasstown Bald and Scotia than at either Egbert or Dorset. Acetylene concentrations are nearly identical at all sites, ranging from 0.58 (Brasstown Bald) to 0.83 (Egbert) in ppbC units. The ethylene concentrations at Brasstown Bald (0.30 ppbC) and Scotia (0.50 ppbC) are substantially lower than those at the other three sites, (0.70-0.93 ppbC). Propene concentrations exhibit greater site-to-site variability, as much as a factor of four from the lowest value (0.05 ppbC) at Scotia to the highest (0.21 ppbC) at Egbert. Greater temporal and spatial variability is to be expected for ethylene and propylene which are more reactive than acetylene toward HO radical by a factor of ≥10 [6].

Alkane (Fig. 2): Several features can be noted in this figure; (1) For the light alkanes from ethane up to n-pentane both absolute concentrations and relative distributions at all sites are very similar, within a factor of two; (2) Values for i-pentane measured at three sites are also seen to be nearly identical; (3) For the heavy alkanes from 2-methyl pentane to n-octane, the median concentrations are much higher, by a factor of three to ten, at Dorset and Egbert than at Brasstown Bald and Scotia, Scotia values being generally the lowest; and (4) both the absolute concentrations and relative abundances of these heavier alkanes are nearly identical at Dorset and Egbert. These observations (1)-(4) may be due in part to the degree of aging of urban air masses transported to these rural sites, the heavier alkanes being generally more photochemically reactive than the lighter alkanes [7].

Aromatic (Fig.3): In general, while the relative abundances of benzene, xylenes and ethylbenzene are similar at all sites, the absolute concentrations of these light aromatic compounds vary significantly from site to site (by a factor of up to 4 for benzene and a factor of ~10 for p- and m-xylenes), the highest values being consistently at Egbert and the lowest at

Scotia. The Scotia data also reveal significantly lower concentrations of xylenes relative to those of benzene and toluene than at the other sites, which may reflect photochemical aging of air masses transported to these sites. For instance, the HO-radical reactivity of xylenes is more than 10 times greater than that of benzene. However, interpretation of these site-to-site variations of median NMHC concentrations clearly requires more detailed information on air mass history for each site. Also, as to be noted in Tables 1-4, the data-set sizes for the aromatics are generally much smaller than those for alkanes at a given site and vary significantly from site-to-site, the largest (≥175 points per compound) being at Scotia and the smallest (≥23 points for o-xylene) at Dorset. Although no bias is apparent toward episodic conditions for data from both Dorset and Egbert, their small sample sizes make statistical comparison with the Scotia data less meaningful.

Natural NMHC (Table 2): The site-to-site variations of natural NMHCs are very large. Namely, median values of isoprene concentrations vary by over a factor of thirty in the ascending order of Egbert (0.84 ppbC), Dorset (3.59 ppbC), Brasstown Bald (12.2 ppbC) and Scotia (25.70 ppbC). Also, isoprene concentrations are shown in this table to be by far the highest in ppbC units among all the natural and anthropogenic NMHC species observed at all four sites, particularly at Brasstown Bald and Scotia. Median concentrations of α- and β-terpene on a carbon basis are approximately 10% of isoprene at Brasstown Bald and less than 1% of isoprene at Scotia. As will be discussed in later, these site-to-site variations in natural NMHC concentrations appear to reflect mainly the differences in the type and the extent of coverage of vegetation at each site as well as the temperature dependence of isoprene emissions from deciduous trees. Among the four measurement sites Egbert is the only site with few deciduous trees in the immediate vicinity, and is therefore expected to be the lowest in isoprene concentrations, in agreement with the observation.

(II) Atmospheric Oxidation Rates of NMHCs

For an assessment of relative importance of individual NMHC species in the formation of oxidants, particularly O_3, their atmospheric oxidation rates, (i.e. removal rates by atmospheric reactants) can provide a more meaningful measure than their actual concentrations. It is well-established that the atmospheric gas-phase oxidation reactions of alkane and aromatic hydrocarbons are initiated mainly by HO radicals, while the olefinic hydrocarbons such as propylene, isoprene and mono-terpenes can be oxidized significantly by both HO radicals and O_3. Rate constants for these relevant reactions are reasonably well known for the ambient temperatures encountered at these ground monitoring sites during the 1988 EMEFS program [7,8]. Thus, rates of reactions consuming the individual hydrocarbons can be calculated from the concentrations of speciated NMHCs observed at various sites (cf. Table 1), in combination with plausible experimental or theoretical values of the ambient concentrations of HO radicals and O_3, which were taken to be 5×10^6 molecule/cm^3 and 100 ppb (i.e. 2.5×10^{12} molecule/cm^3), respectively. These assumed values of HO and O_3 concentrations roughly correspond to those common to highly photochemically active daytime conditions at these rural sites [9,10]. Rates of oxidation thus calculated are plotted in Figure 4 for the twelve most dominant NHMCs. It can be readily noted that isoprene exhibits by far the largest oxidation rate among all NMHC species at all four sites. Also, α- and β-pinene are seen to be the next largest contributors to the overall NMHC oxidation rate at Brasstown Bald and Scotia. Thus, on the average, the natural NMHCs are the main hydrocarbon species responsible for controlling the local atmospheric chemistry at all four site.

For various anthropogenic NMHC types (i.e. alkene, alkane and aromatic), there are observable site-to-site variations in the relative rank of their oxidation rates. Namely, at Scotia the descending order of relative oxidation rates (n-butane = 1.00) is propylene(1.89), n-butane(1.00); i-pentane(0.92), ethylene(0.84), toluene(0.58), propane(0.46), i-butane(0.43), n-pentane(0.43), o-xylene(0.32), and m-, p-xylene(0.32). Thus, the alkene and light alkane compounds exhibit greater atmospheric reactivity than the aromatics at this site. On the other hand, the reactivity ranking at Brasstown Bald is somewhat reversed, the highest being the aromatic compounds, i.e. p-, m-xylene(2.61), toluene(1.70), o-xylene(1.19), n-butane(1.00), propylene(0.70), propane(0.61), n-pentane(0.60), ethylene(0.53), i-butane(0.35) and 2-methyl pentane(0.33). The reactivity trends for the Dorset and Egbert sites are similar to that of Brasstown Bald, but are more pronounced e.g. for Egbert p-, m-xylene(4.26), toluene(1.18), o-xylene(1.39), 2-methyl pentane(1.32), propylene(1.13), ethylene(1.06), i-pentane(1.03), n-butane(1.00), n-heptane(0.96), ethylbenzene(0.78), n-pentane(0.58) and n-hexane(0.43). A similar analysis of atmospheric reactivity ranking has been made recently for urban hydrocarbons [11], based on their median concentrations reported for 39 U.S. cities, i.e. ethylene(3.5), propylene(2.3), 1-butene(2.3), n-hexane(2.2), m, p-xylene(1.4), i-pentane(1.3), 1,2,4-trimethyl benzene(1.8), toluene(1.2), n-butane(1.0), methane(0.7), n-pentane(0.7) and o-xylene(0.5). It appears that the reactivity ranking is somewhat similar, at least qualitatively, for both the urban and rural anthropogenic hydrocarbons.

(III) Daytime Isoprene Concentration Versus Ambient Temperature

Isoprene is emitted primarily by deciduous trees during the daylight hours and, among various factors, its flux is most sensitive to the temperature at the leaf surface [12]. Thus, daytime concentrations of isoprene observed at the four ground sites are expected to be significantly influenced by ambient temperature and solar radiation. Quantitative relationships between natural NMHC source flux and ambient concentration are complex and involve accurate description of both mass transport and chemical production and loss terms. Under certain meteorological conditions a simple box model would provide a reasonable approximation [13,14]. Namely, the following simplified continuity equation describes the conditions that wind speeds are small and vertical mixing is controlled by the planetary boundary layer (PBL) mixing height:

$$(1/x)(dx/dt) = (Q/xh) - k$$

where x = spatial average concentration; Q = spatial average source strength; h = mixing height; k = first order rate constant for the loss of the trace gas; and t = time. This equation reduces to $x = Q/hk$ under a steady state condition, i.e. $dx/dt = 0$, and x is linearly dependent on Q when h and k are approximately constant. Such a situation may occur in the mid-afternoon under high pressure stagnation system. However, extensive data on diurnal mixing height and vertical profiles of natural NMHC concentrations are not available during this study period for all sites.

Site-to-site comparisons of isoprene concentration versus temperature have been made for all site, but only the results from Scotia and Dorset are presented below for illustrative purpose. Fig. 5 shows the Scotia data for sunny periods between 0800 and 1600 EDT, together with our data obtained at Dorset in 1989. The Scotia data represent the most extensive data set obtained at any of the four sites, and clearly demonstrates that the isoprene concentration increases exponentially by more than a factor of ten over the temperature range 15° C to 35° C. Available isoprene flux data for eastern U.S. deciduous trees indicate similar temperature dependence [15]. The 1989 Dorset data are also seen to exhibit similar temperature dependence, although generally lower in concentration than the Scotia data at a given ambient temperature. The isoprene data from Dorset in 1988 are plotted in Figure 6. The solid line in this figure corresponds to the least squares line from the Scotia data (Fig. 5) and the two parallel dashed lines are drawn to encompass all the Scotia data points. The 1988 Dorset data exhibit much larger scattering than those obtained in 1989, with no apparent dependence on wind direction. However, the upper limit values for these Dorset data are seen to coincide with the least squares line for the Scotia data, and the temperature dependence of the overall Dorset data is reasonably well represented by the lower bound line drawn for the Scotia data.

(IV) Correlation Among Anthropogenic NMHCs in Dorset Data

NMHC concentration/time profiles and their relative concentration distributions from the Dorset and Egbert data have been examined in detail to discern any observable trends and patterns indicative of source signatures and also to provide representative NMHC data corresponding to O_3 episodes as an input to the development of explicit chemical mechanism for oxidant modelling.

Summarized in Tables 2(A)-(C) are the values of rank correlation among various NMHCs (listed in Table 1) from Dorset data using Spearman method which is less sensitive to outliers than the more commonly used Pearson method. All the Dorset data are used to derive the correlation coefficients given in Table 2(A), whereas the morning, afternoon and night data were treated separately for the analysis shown in Tables 2(B)-2(C). The shaded boxes contain values ≥ 0.7 which were arbitrarily chosen as a cut off point to indicate a high degree of correlation. The highest correlation coefficient (0.97) in Table 2(A) is seen for n-C_5H_{12} and iso-C_5H_{12}, and this relation is illustrated graphically in Figure 7. Note that both n-C_5H_{12} and iso-C_5H_{12} are not only of combustion origin but also of similar atmospheric reactivity. In general, the light alkanes ($\leq C_6$) exhibit a fair degree of mutual correlation throughout the day. Figure 8 shows actual concentration/time profiles for C_2H_6, C_3H_8, n-C_4H_{10} and i-C_4H_{10} for the afternoon data. It was noted that these profiles for the light alkanes were also closely correlated with that of O_3. On the other hand, the olefinic and aromatic compounds are seen to be very poorly correlated irrespective of the time of the day. Although the exact cause(s) for this divergent behavior is not readily apparent, there are indications that the type and proximity of emission sources as well as atmospheric reactivity are among the probable contributing factors.

CONCLUSION

Data analysis of non-methane hydrocarbon compositions in the C_2-C_{10} range determined during the summer of 1988 at four rural sites in eastern North America, one in northern Georgia, one in central Pennsylvania and two in south-central Ontario, indicates that, although there are significant site-to-site variations of as much as a factor of 10 for some hydrocarbons in terms of median values, a high degree of similarity exists among the relative abundance of the hydrocarbons observed at all sites. The natural NMHC isoprene was the most abundant species in terms of ppbC among all NMHCs observed at all sites, and was primarily responsible for the local formation of oxidants. An extensive dataset for daytime isoprene concentrations at Scotia, Pennsylvania shows a well-defined exponential dependence on ambient temperature, providing a good reference for comparison with more limited isoprene data available from the other sites. Further temporary and spatially resolved data on both natural and anthropogenic hydrocarbons in representative Canadian rural settings are required for an assessment of regional oxidant problem.

ACKNOWLEDGEMENTS

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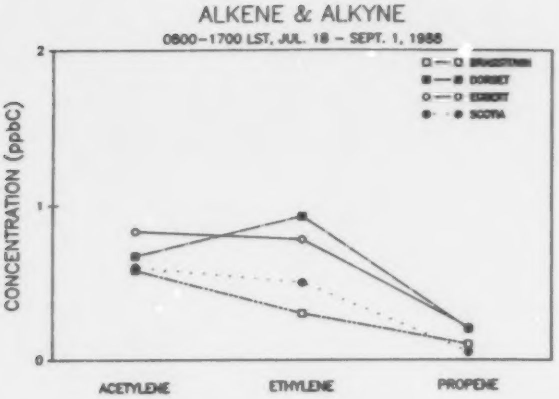


FIGURE 1

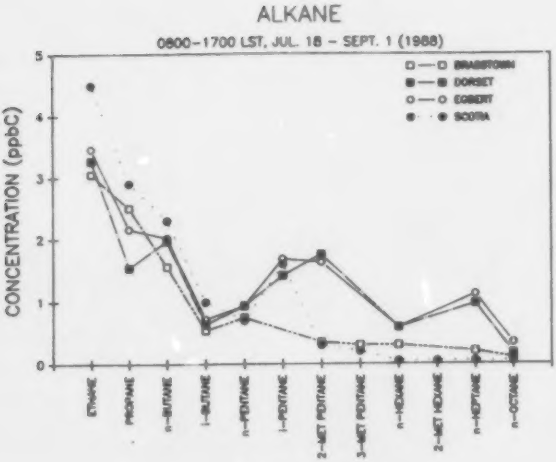
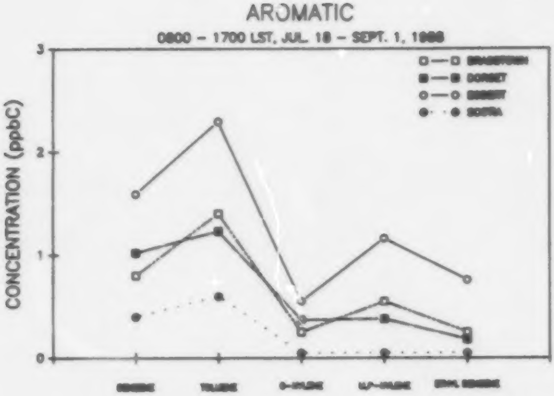


FIGURE 2



FIGUPE 3

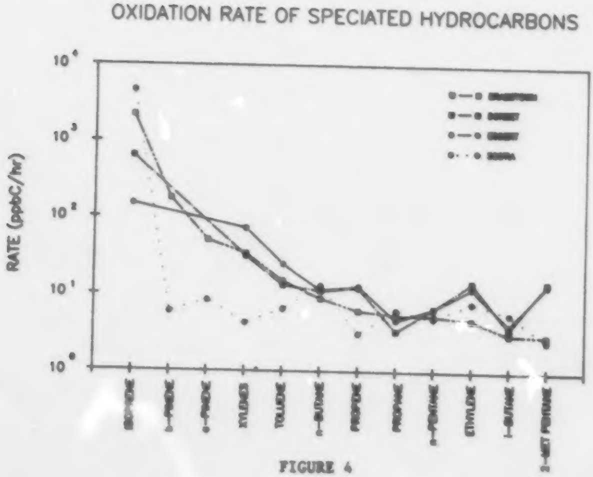


FIGURE 4

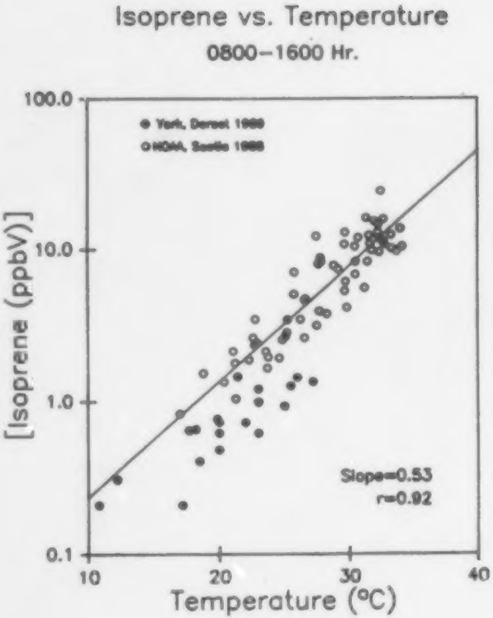


FIGURE 5

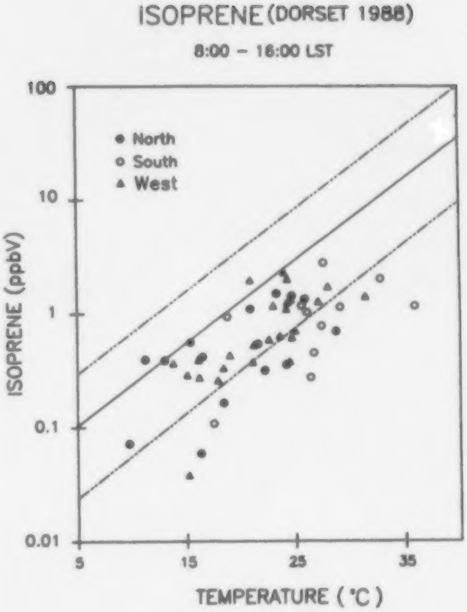


FIGURE 6

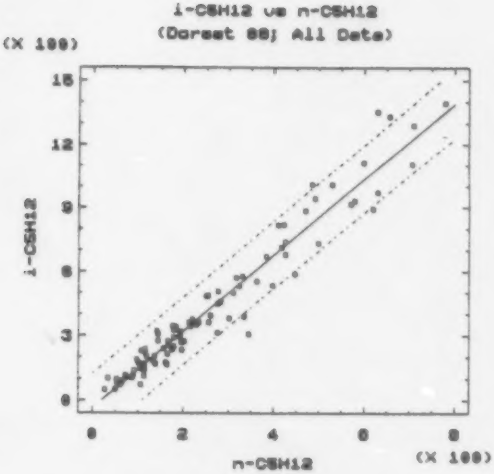


FIGURE 7

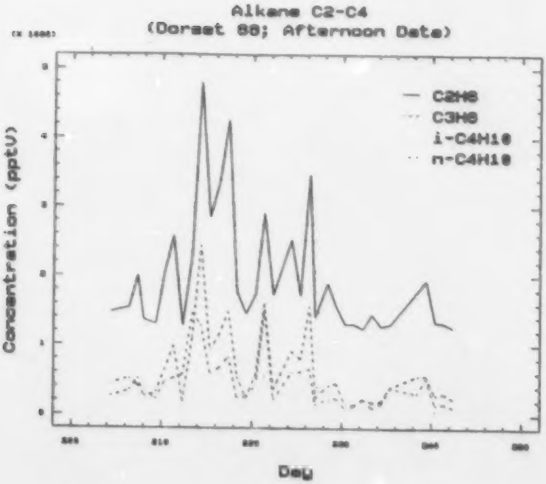


FIGURE 8

Table 1: SUMMARY OF SPECIATED HYDROCARBON CONCENTRATIONS AT RURAL SITES

1988 SUMMER EMEFS HC(ppbc, median) (all data 8:00-17:00 EDT)

Alkyne & Alkene	BRASSTOWN BALD	DORSET	EGBERT	SCOTIA
acetylene	0.58(0.86/0.36)	0.67(0.86/0.50)	0.83(1.29/0.57)	0.60(1.30/0.05)
ethylene	0.30(0.55/0.20)	0.93(1.25/0.70)	0.78(1.19/0.52)	0.50(1.50/0.20)
propene	0.10(0.30/0.10)	0.20(0.25/0.16)	0.21(0.30/0.18)	0.05(0.30/0.05)
Alkane				
ethane	3.05(4.30/1.20)	3.27(3.99/2.91)	3.46(4.78/2.98)	4.50(7.70/2.60)
propane	2.50(3.86/1.15)	1.54(2.21/1.17)	2.16(3.48/1.36)	2.90(5.40/1.30)
n-butane	1.56(2.98/0.91)	1.97(2.84/1.32)	2.02(3.01/1.35)	2.30(4.20/1.10)
i-butane	0.54(0.90/0.48)	0.64(0.99/0.44)	0.72(1.36/0.50)	1.00(1.90/0.40)
n-pentane	0.75(1.65/0.40)	0.94(1.28/0.72)	0.94(1.36/0.52)	0.70(1.30/0.40)
i-pentane		1.42(1.90/1.16)	1.68(2.59/0.83)	1.60(3.30/0.90)
2-met pentane	0.35(0.90/0.20)	1.75(2.20/1.92)	1.63(2.11/0.97)	0.30(0.70/0.05)
3-met pentane	0.30(0.65/0.15)			0.20(0.40/0.05)
n-hexane	0.30(0.50/0.20)	0.59(0.81/0.47)	0.59(0.87/0.40)	0.05(0.40/0.05)
n-heptane	0.20(0.45/0.10)	0.97(1.54/0.60)	1.12(1.72/0.64)	0.05(0.05/0.05)
n-octane	0.20(0.55/0.05)	0.17(0.34/0.12)	0.34(0.51/0.14)	0.05(0.05/0.05)
Aromatic				
benzene	0.80(1.25/0.55)	1.02(1.31/0.75)	1.59(2.68/0.98)	0.40(1.10/0.20)
toluene	1.40(3.05/0.90)	1.23(1.79/0.93)	2.29(3.92/0.78)	0.60(1.60/0.30)
o-xylene	0.25(0.60/0.15)	0.37(0.55/0.20)	0.55(0.78/0.37)	0.05(0.30/0.05)
p,m-xylene	0.55(1.40/0.30)	0.38(0.55/0.31)	1.16(1.84/0.55)	0.05(0.50/0.05)
ethylbenzene	0.25(0.50/0.15)	0.20(0.37/0.17)	0.76(1.10/0.68)	0.05(0.30/0.05)
Natural				
isoprene	12.20(25.70/3.20)	3.59(5.77/2.34)	0.84(1.47/0.59)	25.70(44.30/8.10)
α-pinene	0.30(25.70/3.20)			0.05(0.20/0.05)
β-pinene	1.50(4.95/0.25)			0.05(0.20/0.05)

Values in parentheses correspond to +/- 67 % of the data ranges.

TABLE 2(A)

RANK CORRELATION : Dorset 88 (All Data)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.46	0.75	0.47	0.77	0.63	[illegible]	0.57	0.62	0.54	0.62	0.24	0.20	0.04	0.29
C2H4	0.46	1.00	0.31	0.57	0.35	0.31	0.29	0.46	0.42	0.38	0.41	0.09	0.19	-0.08	0.25
C2H6	0.75	0.31	1.00	0.30	0.86	0.63	0.72	0.46	0.53	0.40	0.49	0.15	0.15	0.24	0.14
C3H6	0.47	0.57	0.30	1.00	0.39	0.49	0.43	0.64	0.60	0.54	0.51	0.25	0.29	-0.13	0.35
C3H8	0.77	0.35	0.86	0.39	1.00	[illegible]	[illegible]	0.64	[illegible]	0.52	0.61	0.21	0.35	0.14	0.38
n-C4H10	0.63	0.31	0.63	0.49	[illegible]	1.00	[illegible]	[illegible]	[illegible]	0.64	0.78	0.20	0.53	0.10	0.58
i-C4H10	[illegible]	0.29	0.72	0.43	0.86	0.96	1.00	0.83	[illegible]	0.63	0.78	0.22	0.50	0.12	0.51
n-C5H12	0.57	0.46	0.46	0.64	0.64	0.88	[illegible]	1.00	[illegible]	0.78	0.81	0.34	0.65	0.06	0.76
i-C5H12	0.62	0.42	0.53	0.60	0.70	0.96	[illegible]	0.97	1.00	0.76	0.86	0.29	0.61	0.07	0.71
n-C6H14	0.54	0.38	0.40	0.54	0.52	0.64	0.63	0.78	[illegible]	1.00	0.75	0.27	0.57	-0.01	0.52
i-C6H14	0.62	0.61	0.49	0.51	0.61	0.78	[illegible]	0.81	[illegible]	0.75	1.00	0.21	0.53	0.16	0.72
BENZENE	0.24	0.09	0.15	0.25	0.21	0.20	0.22	0.34	0.29	0.27	0.21	1.00	0.24	0.15	0.32
TOLUENE	0.20	0.19	0.15	0.29	0.35	0.53	0.50	0.65	0.61	0.57	0.53	0.24	1.00	0.38	0.63
o-XYL	0.04	-0.08	0.24	-0.13	0.14	0.10	0.12	0.06	0.07	-0.01	0.16	0.15	0.38	1.00	0.52
m,p-XYL	0.29	0.25	0.14	0.35	0.38	0.58	0.51	0.76	0.71	0.52	0.72	0.32	0.63	0.52	1.00

TABLE 2(B)

Dorset 88 (Morning Data)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.60	[illegible]	0.57	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.71	0.62	0.31	-0.02	0.25
C2H4	0.60	1.00	0.52	0.66	0.62	0.53	0.54	0.62	0.58	0.43	0.48	0.38	0.22	-0.04	0.22
C2H6	[illegible]	0.52	1.00	0.44	0.89	0.67	[illegible]	0.64	0.66	0.64	0.72	0.57	-0.06	0.37	0.24
C3H6	0.57	0.66	0.44	1.00	0.54	0.54	0.51	0.67	0.61	0.53	0.46	0.19	0.27	-0.04	0.16
C3H8	[illegible]	0.62	[illegible]	0.54	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.75	0.70	0.16	0.29	0.39
n-C4H10	[illegible]	0.53	0.67	0.54	0.76	1.00	[illegible]	[illegible]	[illegible]	0.69	0.82	0.64	0.36	0.01	0.56
i-C4H10	[illegible]	0.54	[illegible]	0.51	[illegible]	0.96	1.00	0.92	[illegible]	0.73	0.84	0.73	0.35	0.05	0.56
n-C5H12	[illegible]	0.62	0.64	0.67	0.79	0.91	[illegible]	1.00	[illegible]	0.75	0.80	0.70	0.48	-0.02	0.58
i-C5H12	[illegible]	0.58	0.66	0.61	0.80	[illegible]	[illegible]	[illegible]	1.00	0.75	0.84	0.71	0.45	-0.08	0.63
n-C6H14	[illegible]	0.43	0.64	0.53	0.71	0.69	[illegible]	0.76	[illegible]	1.00	[illegible]	0.47	0.37	0.01	0.49
i-C6H14	[illegible]	0.48	[illegible]	0.46	0.75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	0.50	0.46	0.15	[illegible]
BENZENE	0.62	0.38	0.57	0.19	0.70	0.64	[illegible]	0.70	[illegible]	0.47	0.50	1.00	0.27	-0.09	0.18
TOLUENE	0.31	0.22	-0.06	0.27	0.16	0.36	0.35	0.48	0.45	0.37	0.46	0.27	1.00	0.01	0.51
o-XYL	-0.02	-0.04	0.37	-0.04	0.29	0.01	0.05	-0.02	-0.08	0.01	0.15	-0.09	0.01	1.00	0.46
m,p-XYL	0.25	0.22	0.24	0.16	0.39	0.56	0.56	0.58	0.63	0.49	[illegible]	0.18	0.51	0.46	1.00

TABLE 2(C)

RANK CORRELATION: Dorset 88 (Afternoon Data)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.29	[illegible]	0.41	[illegible]	[illegible]	[illegible]	0.55	0.69	0.54	0.69	-0.27	0.01	0.25	0.42
C2H4	0.29	1.00	0.20	0.58	0.18	0.30	0.27	0.41	0.42	0.58	0.38	-0.40	0.04	-0.02	0.17
C2H6	[illegible]	0.20	1.00	0.50	[illegible]	[illegible]	[illegible]	0.61	0.69	0.54	0.58	-0.14	0.02	0.47	0.23
C3H6	0.41	0.58	0.50	1.00	0.42	0.59	0.56	0.99	0.63	0.54	0.35	0.05	0.00	-0.25	0.18
C3H8	[illegible]	0.18	[illegible]	0.42	1.00	[illegible]	[illegible]	0.64	[illegible]	0.56	0.66	-0.31	0.30	0.41	0.49
n-C4H10	[illegible]	0.30	0.75	0.59	[illegible]	1.00	[illegible]	[illegible]	[illegible]	0.62	[illegible]	-0.41	0.40	0.00	[illegible]
i-C4H10	[illegible]	0.27	[illegible]	0.56	[illegible]	[illegible]	1.00	0.78	[illegible]	0.62	[illegible]	-0.33	0.34	0.51	[illegible]
n-C5H12	0.55	0.41	0.61	0.59	0.64	[illegible]	0.78	1.00	0.92	[illegible]	0.57	-0.40	0.34	0.20	[illegible]
i-C5H12	0.69	0.42	0.69	0.63	[illegible]	[illegible]	[illegible]	[illegible]	1.00	0.63	[illegible]	-0.40	0.34	0.49	[illegible]
n-C6H14	0.54	0.58	0.54	0.54	0.56	0.62	0.62	[illegible]	0.63	1.00	0.56	-0.31	0.42	0.23	0.18
i-C6H14	0.69	0.38	0.58	0.35	0.66	[illegible]	[illegible]	0.57	[illegible]	0.56	1.00	-0.54	0.18	0.41	0.41
BENZENE	-0.27	-0.40	-0.14	0.05	-0.31	-0.41	-0.33	-0.40	-0.40	-0.31	-0.54	1.00	-0.22	0.20	-0.25
TOLUENE	0.01	0.04	0.02	0.00	0.30	0.40	0.34	0.34	0.34	0.42	0.18	-0.22	1.00	0.57	0.56
o-XYL	0.25	-0.02	0.47	-0.25	0.41	0.00	0.51	0.20	0.49	0.23	0.41	0.20	0.57	1.00	[illegible]
m,p-XYL	0.42	0.17	0.23	0.18	0.49	[illegible]	[illegible]	[illegible]	[illegible]	0.18	0.41	-0.25	0.56	[illegible]	1.00

TABLE 2(D)

Dorset 88 (Night Data)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	i-C6H14	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.36	0.66	0.33	0.63	[illegible]	[illegible]	0.53	0.63	0.95	0.50	0.26	0.26	-0.26	-0.13
C2H4	0.36	1.00	0.28	0.41	0.28	0.32	0.25	0.42	0.42	0.22	0.40	0.35	0.24	0.01	0.39
C2H6	0.66	0.28	1.00	0.01	[illegible]	0.68	[illegible]	0.40	0.53	0.32	0.32	0.01	0.39	0.01	0.07
C3H6	0.33	0.41	0.01	1.00	0.13	0.29	0.18	0.53	0.65	0.27	0.51	0.55	0.18	-0.10	0.35
C3H8	0.63	0.28	[illegible]	0.13	1.00	[illegible]	[illegible]	[illegible]	[illegible]	0.99	0.61	0.00	0.65	0.08	0.36
n-C4H10	0.71	0.32	0.68	0.29	[illegible]	1.00	[illegible]	[illegible]	[illegible]	0.67	[illegible]	0.02	0.68	0.15	0.52
i-C4H10	0.75	0.25	[illegible]	0.18	[illegible]	[illegible]	1.00	[illegible]	[illegible]	0.67	[illegible]	-0.04	0.67	0.06	0.42
n-C5H12	0.53	0.42	0.40	0.53	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	0.29	[illegible]	0.07	[illegible]
i-C5H12	0.63	0.42	0.53	0.65	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	0.16	[illegible]	0.27	0.67
n-C6H14	0.95	0.22	0.32	0.27	0.59	0.67	0.67	[illegible]	[illegible]	1.00	[illegible]	0.16	[illegible]	-0.27	0.57
i-C6H14	0.50	0.40	0.32	0.51	0.61	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	0.22	[illegible]	0.11	[illegible]
BENZENE	0.26	0.35	0.01	0.55	0.00	0.02	-0.04	0.29	0.16	0.16	0.22	1.00	0.05	-0.12	0.13
TOLUENE	0.26	0.24	0.39	0.18	0.65	0.68	0.67	[illegible]	[illegible]	[illegible]	[illegible]	0.05	1.00	-0.03	0.65
o-XYL	-0.26	0.01	0.01	-0.10	0.08	0.15	0.06	0.07	0.27	-0.27	0.11	-0.12	-0.03	1.00	0.51
m,p-XYL	-0.13	0.39	0.07	0.35	0.36	0.52	0.42	[illegible]	0.67	0.57	[illegible]	0.13	0.65	0.51	1.00

A14

ATMOSPHERIC TRACE GAS MEASUREMENTS USING A TUNABLE DIODE LASER ABSORPTION SPECTROMETER

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INTRODUCTION

The Eulerian Model Evaluation Field Study (EMEFS) was designed to provide sufficient data to allow a full evaluation of computer models of the atmosphere over Northeastern North America. The major thrust was in the evaluation of the two state-of-the-science Eulerian models being used to simulate and study the chemistry of acid deposition and oxidant formation. They are the Acid Deposition and Oxidants Model (ADOM) (Venkatram et al. 1988), supported by the Ministry of the Environment, the Atmospheric Environment Service of Environment Canada, the Electric Power Research Institute (EPRI), and Umweltbundesamt (West Germany) and The Regional Acid Deposition Model (RADM) (Chang et al. 1987) supported by the Environmental Protection Agency (EPA). These models include our current best understanding of the sources of gases to the atmosphere, the best available three dimensional meteorology, the most complete gas and aqueous phase chemistry available, and our best measurements of trace gas concentrations. Realizing the importance of the predictions of these models, it was deemed necessary to establish their credibility by comparison with data collected during EMEFS.

The Canadian component of the field study involved data collection from the MOE-APIOS and AES-CAPMoN networks. In addition, two sites were designated as intensive or enhanced sites. These were the AES site at Egbert (near Barrie) and the Ministry site at Dorset. The purpose of these sites was to obtain data using enhanced techniques that required operation by specially trained personnel or at a frequency not possible under normal operating conditions.

While the field study was put in place for model evaluation it became clear that the data obtained, especially that from the enhanced sites, could also be used to address a number of additional issues. The Canadian Institute for Research in Atmospheric Chemistry (CIRAC) took the lead in the co-ordination of the Canadian Air Chemistry Experiment (CACE) which aimed to ensure the collection of a complete data set capable of addressing some specific atmospheric chemistry questions. The work performed under this grant had as its focus the EMEFS program but we were always mindful of the objectives of CACE.

We undertook a measurement program at the Ministry site at Dorset to measure the concentrations of a number of key species in the atmospheric oxidation cycle. In this paper we use some of the data obtained, during a field campaign in the summer of 1989, to investigate the importance of some site specific effects on the chemical composition of the atmosphere. The ability to distinguish between such local effects and larger scale changes in atmospheric composition is necessary if we are to continue to improve our understanding of the chemistry of the atmosphere.

MEASUREMENTS

The following is a listing of the chemical species that were measured at the Dorset site, and a brief description of the techniques used.

Hydrogen Peroxide and Formaldehyde using a Tunable Diode Laser Absorption Spectrometer (Schiff et al. 1983, 1987, Harris et al 1990, and Slemr et al. 1986)

NO and NO_y using an in-house fabricated, high sensitivity chemiluminescent NO analyser similar to that used by Misanchuk et al. (1987). This was equipped with a gold converter for NO_y measurements (Fahey et al. 1986).

Ozone using a commercial UV absorption ozone analyzer (Dasibi Model 1003-AH).

NO_2 and NO_x using two modified commercial luminol NO_2 analyzers (Unisearch/Scintrex LMA-3) to measure NO_2 directly and NO_x (NO + NO_2) by use of a CrO_3 converter (Drummond et al. 1990).

Solar radiation using a U.V. radiometer (Eppley Labs 280-320nm).

Basic meterological parameters using a commercial meteorological system (MetOne) for wind speed, wind direction, temperature and humidity.

Boundary layer heights up to 500 meters were obtained by Ontario Hydro using an acoustic sounder.

CASE STUDY: THE NIGHT OF JULY 2 1989

We have chosen this night as the case study as the two days seem to be similar and there is a clear nocturnal inversion leading to some interesting observations.

There was a stable high pressure system over the site. The daytime temperature maximum for both days was 29°C with the nighttime minimum of 9°C. The radiation measurements for both days showed they were relatively cloud free. The wind velocities during the daylight hours were stable at around 4-6 km/hr from the west, but dropped to below 1 km/hr and shifted to be almost from the north for most of the night.

As expected under these conditions a strong nighttime radiation inversion was formed. The acoustic sounder first indicated a developing inversion at 1945. By 2215 this had developed into a very strong stable surface based inversion whose depth varied from 80 to 200 meters with an average of 150 meters. The lower temperature and trapping of the air close to the surface brought relative humidities to the saturation level as evidenced by our sensor recording relative humidities over 100%

for the duration of the strong inversion. This inversion began to lift at 0915, three hours after first light. There was evidence of a 200 meter thick rising dissipating elevated inversion for an additional next half hour before the inversions finally dissipated and the normal daytime thermal activity dominated the first 500 meters of the atmosphere.

Knowing the height of this nocturnal inversion is extremely important in interpreting data from this site. It is in a shallow valley with hills within a kilometre in three directions. The highest points on each of these hills are 67, 69 and 89 meters above the site. These data show that the nighttime inversion reaches above these hills so the site is not completely isolated at night. There is still the possibility of horizonal transport under the inversion although in this case the low wind speeds would preclude very much transport. This sounder data is supported by a single night of ozone measurements where the ozone measured on the top of the highest hill was identical to that measured at the site. Thus we must conclude that the nighttime measurements made at the site are representative of the surface for the surrounding area.

The chemical and meteorological data are plotted in the Figures. Figure 1 shows the height of the inversion and the U.V. solar irradiance. The inversion developed slowly after U.V. sunset and persisted well after sunrise. The very low heights in the early evening were from the weak developing inversion, the strong inversion commenced at about 10 pm. Figure 2 shows the relative humidity and wind speed data. High humidities and low wind speeds were associated with the strong inversion. Thus the aqueous phase become increasingly important and the amount of horizontal transport was small.

Figure 3 shows the NO_x and ozone data. Ozone showed a strong diurnal variation. The maximum concentration for both days was 90 ppbv a value indicative of strong photochemical activity. The concentration began to fall at 1945 coincident with the onset of the inversion. The concentration droped all night to a minimum of 25 ppbv at 0445 but when the inversion broke up at 915 the ozone rose quickly and when the last of the inversion dissipated at 0945 the ozone concentration was back up to 68 ppbv and reached 80 within half an hour. The ozone trapped below the inversion was clearly lost during the night whereas the ozone aloft, which was mixed back to the surface following the breakup of the inversion, was not. The ozone could have been lost by reaction or deposition to the surface. There was no indication of an NO source in the area and the emission of reactive hydrocarbons at these low temperatures is expected to be low thus deposition to the surface is the most likely fate of the ozone. The ozone concentration shows an exponential decay and if we assume an inversion depth of 150 meters, the deposition velocity calculated from the decrease in ozone over the 9 hours of the inversion is $0.55 \pm .02$ cm s^{-1}. This is consistent with the commonly accepted value of approximately 0.5 cm s^{-1}. NO_x, the sum of NO and NO_2 showed a similar decay to that of ozone indicating a similar deposition velocity.

Hydrogen peroxide and formaldehyde are shown in Figure 4. Hydrogen peroxide, which had averaged 2 ppbv during the afternoon, dropped precipitously as the inversion formed. This removal was too fast to be a surface process and was more likely an absorption of hydrogen peroxide into the rapidly growing aqueous phase as the temperature dropped and the humidity increased. The hydrogen peroxide appeared again with the breakup of the inversion bringing dryer air from aloft. Formaldehyde exhibited a complex behaviour as it appeared to increase as the inversion formed and there was some deposition loss with a deposition velocity of about 0.2 cm s^{-1}. The concentration rose again as the inversion broke up.

CONCLUSION

We have identified a night in which there was a strong nocturnal inversion and that this had some interesting chemical consequences. We are able to use them to examine both physical and chemical processes that are occurring. The data could now be compared directly with nocturnal boundary layer models. Finally the removal of such local effects will ensure the remaining data will be representative of the region and provide a good data set against which to evaluate models.

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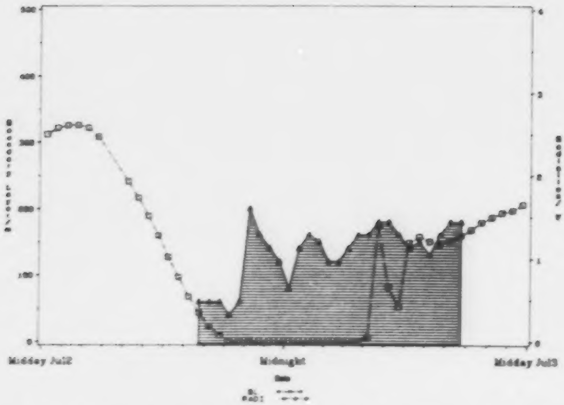

FIGURE 1: U.V. Radiation and boundary layer height as measured at the Dorset site on the night of July 2 1989.

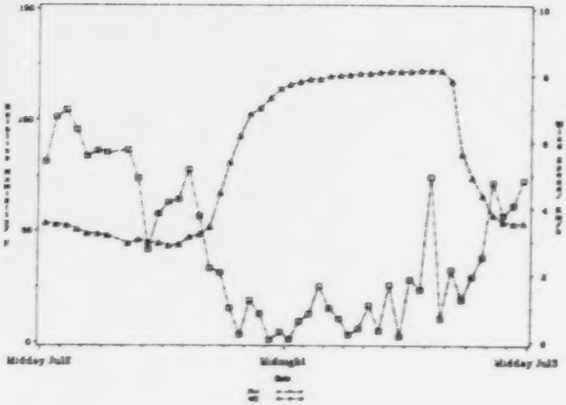

FIGURE 2. Relative Humidity and Wind Speed measured for the same conditions as Figure 1

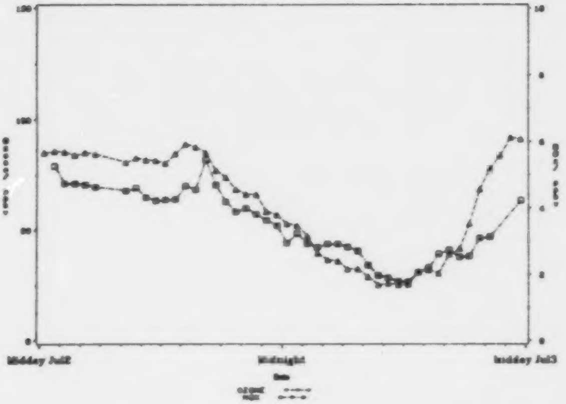

FIGURE 3: Ozone and NO_x as measured for the same conditions as Figure 1

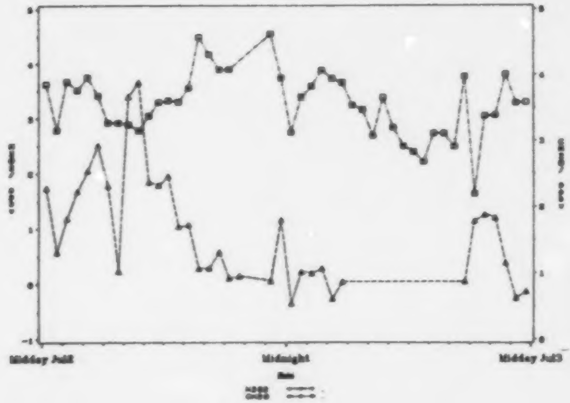

FIGURE 4: Formaldehyde and Hydrogen Peroxide as measured for the same conditions as Figure 1

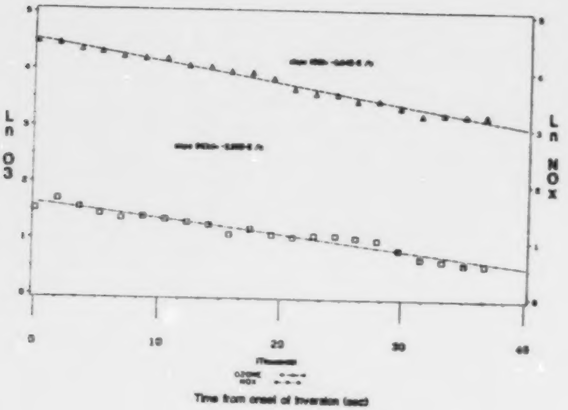

FIGURE 5: Regression plots of Ln(ozone) and ln(NO_x) against the duration of the strong nocturnal inversion.

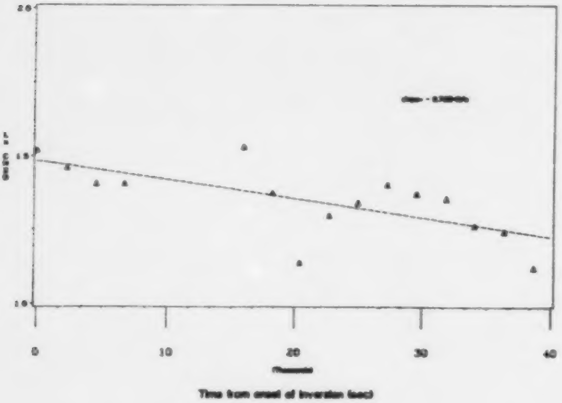

FIGURE 6: Same as Figure 5 but for formaldehyde.

A15

UPTAKE AND DISTRIBUTION OF NAPHTHALENE IN VEGETABLE PLANTS FOLLOWING FOLIAR AND ROOT EXPOSURE

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Abstract

For the purposes of risk analysis, it is desirable to determine dose-response relationships describing the growth response to and tissue accumulation of organic pollutants, relative to various environmental parameters. This paper describes preliminary results of a study, the objectives of which are to relate foliar and root exposures of various vegetable species to naphthalene/naphthol, to growth and tissue concentration responses, as they relate to soil type. This study utilizes a central composite factorial experimental design and analysis of covariance to enhance the collection and interpretation of data. The first experiment demonstrated that growth response to naphthol was more strongly related to soil type (as described by cation exchange capacity) than to applied concentration. Regression analysis indicated that the shape of the response was positive linear and negative quadratic, indicating that as CEC increases, growth reduction by soil naphthol is increasingly diminished. An experiment into plant response to atmospheres containing naphthalene suggests that species type is a strong determinant of tissue accumulation; these results however, are very preliminary and require confirmation.

Introduction

The phytotoxicity and potential for contamination of vegetables by organic compounds of industrial origin is of increasing concern to members of both public and private sectors. While a considerable data base on the uptake and accumulation of agricultural organic chemicals by vegetation exists, a similar data base for industrial organic compounds is scanty. The information on agricultural chemicals cannot be readily transferred to industrial contaminants, as the molecular characteristics of the two groups of compounds are quite different. The uptake of organic compounds from soil or air by plants is dependent on numerous parameters, including the size and water solubility of the compound, and the tendency of the compound to adhere to soil particles. This latter characteristic is to a large extent dependent on the soil type, in particular the amount of organic material, and the relative tendency of a soil to sequester organic molecules may be indicated by the cation exchange capacity (CEC). Due to the wide range of soil types which may be encountered in a natural or agricultural ecosystem, it is desirable that dose-response relationships be developed to describe the response of plants to ranges of contaminant concentration and soil types. The objectives of this project are to determine dose-response expressions which relate concentration of naphthalene or naphthol applied to the soil or the air surrounding the plant and cation exchange capacity of the rooting medium, to growth and tissue naphthalene concentration of tomato (*Lycopersicon esculentum* cv. New Yorker), radish (*Raphanus sativus* cv. Cherry Belle) and swiss chard (*Beta vulgaris* cv. White King). The dose response relationships are to be determined using: an incomplete factorial experimental design known as a partial central composite; analysis of covariance for the reduction of plant-to-plant variation; and polynomial regression for description of the relationship (Marie and Ormrod, 1986; Ormrod et *al*., 1984).

Materials and Methods

Seeds were sown in either Promix BX (high cation exchange capacity), a mixture of sand and Promix BX (low cation exchange capacity) or a mixture of vermiculite and Promix BX (medium cation exchange capacity), at a rate of three seeds per pot. The pots were then placed in a controlled environment chamber which delivered a day/night temperature regime of 25/20°C, each for 12h, canopy level photosynthetically active radiation at 325 $\mu E\ m^{-2}s^{-1}$ for a 16h photoperiod and 70% relative humidity (Ormrod et *al*., 1980). Planting was staggered in order that germination of all three species occurred on approximately the same day. Three days after germination, seedlings were thinned to one per pot, and the plants were grown for three more weeks. During this period, they were irrigated with half-strength Hoagland's nutrient solution as required, when the soil appeared dry. On day 22, planar leaf area of swiss chard and radish, and plastochron index of tomato, were estimated for use in analysis of covariance.

Following covariate measurement, the plants were placed in exposure cubes with environmental conditions similar to those in the controlled environment growth chambers. Two ml of naphthol or naphthalene in ethanol were applied to the soil; plants were harvested on the third day after application of the contaminant. Foliar injury, as well as fresh and dry weights of shoot (divided into stem, leaf and hypocotyl where applicable) and leaf area were assessed on the plants. Exposure of shoots to air containing naphthalene was accomplished by constructing large permeation tubes through which air was passed and then metered into the main air stream entering the exposure chambers. Alteration of the rate of air flow through the permeation tube with a flowmeter controlled the concentration of naphthalene in the chamber. Determination of exposure concentration was by gas chromatography, using manual injection; samples were taken hourly during the five days of exposure. At the end of the exposure, analysis of naphthalene concentration in plant tissues was determined; since the tissue was not washed prior to analysis, the values represent surface adsorption as well as absorption.

The experimental design was a partial central composite, with seven contaminant concentration/soil CEC combinations (Figure 1). The central treatment (CEC=med, naphthol/naphthalene concentration=10 mg/l) is repeated twice for each replication of the other points, in order that all areas of the response surface have approximately equal estimates of variance. The treatment means were summarized by polynomial functions in the second order for both factors, including an interaction term.

Results

Preliminary results (first two of four replications) indicated that there was differentiation among the treatment means for each species exposed to naphthol via the soil (Table 1). When the data (which are summarized in Table 1) were subjected to regression analysis, most growth parameters were related to CEC more strongly than to concentration of naphthol (Table 2). For all growth parameters, a significant portion of the total sum of squares was accounted for by the covariate, indicating that a significant reduction in error sum of squares was realized, leading to improved precision of the experiment (data not shown). This contribution of analysis of covariance to the detection of plant response has been noted for gaseous air pollutant studies (Ormrod *et al.*, 1983). Also not shown are the data for growth response of radish hypocotyl and tomato stem, for which there was little of significance, mainly due to large variation in the data. It should also be noted that naphthalene caused very little growth response in these three species, likely due to its low solubility in water; those results are not reported here.

Tissue concentrations of naphthalene from the first replication of the experiment in which the plant shoot was exposed to atmospheres containing various concentrations of naphthalene, demonstrated no consistent effect of soil type, but were related to exposure concentration and species (Table 3). Tomato shoot had the highest tissue concentrations of naphthalene at all exposure concentrations, while the other two shoot types had similar tissue concentrations, relative to exposure concentration. Radish root data were similar to that for radish shoot.

Discussion

Although Table 1 indicates that both concentration of naphthol and cation exchange capacity of the rooting medium are related to growth response of these species to this compound, it is clear from the regression analysis in Table 2 that CEC is the more important determinant of growth response to naphthol in the soil, and that there is little interaction between these two factors in those responses. This suggests that the concentration of compound available to the plant is determined more by soil type than by the applied dose, within the ranges of the two factors utilized in this study. Finalization of the dose response relationships, in the form of quantification of the polynomial coefficients, will further characterize the relative importance of the linear and quadratic components. When plant shoots were exposed to atmospheres containing naphthalene, tissue concentration was independant of soil type, as could be expected. However, it was related to exposure concentration and plant species; this latter factor probably relates to the affinity of the leaf surface for the compound (i.e. the presence of trichomes or cuticular waxes). It is clear from these data that greater separation of treatment concentrations is required for the establishment of dose-response relationships.

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Figure 1: Treatment combinations for partial central composite rotatable experimental design.

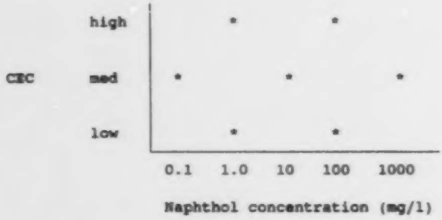

Table 1: Treatment means for growth response of tomato, radish and swiss chard grown in rooting media with different CEC's, to various concentrations of naphthol.

CEC	low		med			high	
[nap]	1.0	100	0.1	10	1000	1.0	100
Tomato							
LFW	2.27	2.43	3.16	2.39	1.76	2.67	2.08
LDW	.211	.251	.305	.240	.216	.249	.232
LA	87.8	94.7	118	90.3	60.7	101.3	74.9
Radish							
LFW	3.96	4.12	6.95	5.35	4.63	6.04	5.22
LDW	.416	.409	.554	.452	.533	.432	.468
LA	107	111	174	141	124	161	142
Swiss chard							
SFW	3.21	2.25	4.16	5.29	1.66	4.05	3.61
SDW	.246	.263	.306	.334	.220	.272	.299
SA	64.0	48.2	84.0	102	46.9	83.3	76.9

LFW and LDW are leaf fresh and dry weights, respectively, the units of which are g/plant. SFW and SDW are shoot fresh and dry weights, respectively, the units of which are g/plant. LA and SA are leaf and shoot area, respectively, the units of which are cm^2/plant.

Table 2: Polynomial coefficients which describe the relationships between growth of tomato, radish and swiss chard, and CEC of rooting media and concentration of naphthol.

	CEC	[nap]	CEC x [nap]
Tomato			
LFW	+L, -Q	ns	-
LDW	+L, -Q	ns	ns
LA	+L, -Q	ns	ns
Radish			
LFW	+L, -Q	ns	ns
LDW	+L, -Q	ns	ns
LA	+L, -Q	ns	ns
Swiss chard			
SFW	+L, -Q	ns	ns
SDW	+L, -Q	+L, -Q	ns
SA	+L, -Q	ns	ns

+L indicates linear coefficient with a positive sign;
-Q indicates quadratic coefficient with a negative sign;
- indicates negative interaction;
ns indicates no significant regression coefficients;
linear and quadratic coefficients significant at $P \leq 0.10$.

Table 3: Treatment means for tissue concentration of tomato, radish and swiss chard grown in media with different CEC's and exposed via the atmosphere to various concentrations of naphthol.

Species	Exposure Concentration (ng/cc)			
Soil Type	12	14	19	65
Swiss Chard shoot				
P + S	.03	.01	.03	.16
P + V	.02	.02	n.d.	.11
P	.06	.06	.04	.18
Tomato shoot				
P + S	.48	.26	n.a.	2.20
P + V	.42	.25	.16	2.30
P	.14	.22	.21	1.10
Radish shoot				
P + S	.09	.03	.03	.16
P + V	.04	.03	.21	.30
P	.05	.03	.05	.30
Radish hypocotyl				
P + S	.02	.01	.02	.10
P + V	.02	n.d.	.02	.11
P	.05	n.d.	n.d.	.13

P + S indicates Promix/sand mixture;
P + V indicates Promix/vermiculite mixture;
P indicates Promix used alone;
n.d. indicates below limit of detection;
n.a. indicates not available

PHYTOTOXICITY OF URANIUM

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ABSTRACT

The literature offers conflicting information on the phytotoxicity of uranium (U). Levels as low as 5 mg U/kg soil, well within the normal background range, have been cited as toxic, whereas many studies report no toxicity at levels 100- to 1000-fold higher. Uranium in soil does not often present a radiological hazard to humans, but toxicity to plants could lead to prescribed cleanup and assessment criteria for industrial activities. This study was designed to identify the concentration of soil U at which plant performance is affected. Although the results here are expressed relative to total soil U, measures of soil-extractable U and plant U concentrations are pending. Nine levels of U were added to background-level soils. Beans were grown to maturity in an outdoor lysimeter study with two soils. Germination tests in the growth chamber were done with eleven soils and with five plant species. A rapid cycling *Brassica rapa* cultivar, proposed as a new toxicity test subject, was also grown to maturity on two of the soils in the growth chamber. Preliminary observations indicate little or no effect of concentrations below 300 mg U/kg soil. Results from the seed germination experiments only are presented in this preliminary report.

INTRODUCTION

A recent literature review highlighted the deficiencies of data on uranium (U) toxicity to plants (Sheppard 1989). Several papers reported toxicity at near background levels, below 10 mg U/kg soil. The concern with these papers, although they have been cited by various agencies (Hanson 1980, Inland Waters Directorate 1983, Beak Consultants Ltd. 1987), is that their findings are difficult to confirm. One is a review of German research prior to 1927 (Stoklasa and Penkava 1928), and interpretation is made difficult by the use of archaic units of measure and uncertain methods. The others are more recent (Zhukov and Zudilkin 1971, Bufatin et al. 1986, Shevchenko et al. 1987) and describe what appear to be reasonable pot culture experiments. However, interpretation is again hampered by the lack of ancillary information. In contrast to these, there are numerous, better-supported reports of no toxic effects at much higher U levels (see Sheppard 1989).

This discrepancy in the literature must be resolved. At present it is not clear whether U toxicity to plants occurs at the concentrations found in some Ontario soils. Phytotoxicity of U may be an important criteria for remediation in areas such as around Port Hope. As a result, this study was undertaken.

The results presented in this report do not include the entire study. In particular, results from the outdoor, full maturity experiment, and of U analyses in soils and plants, are pending.

METHODS AND MATERIALS

Soil Collection, Preparation and U Analyses

Eleven soils were chosen to represent a broad range of edaphic variables (Table 1), and to represent background-level soils from regions in Canada where high levels of soil U are found. About 600 L of the agricultural (A), boreal forest (B) and garden (G) soils, and 60 L of the other soils, were collected. They were partially dried to a workable moisture content and sieved to pass a 0.5-cm mesh. After thorough mixing, each soil was stored in sealed plastic pails. Whenever soil was taken from these pails, the moisture content was determined, and all analyses and treatments were based and are presented on an oven-dried moisture content (105°C for 24 h).

TABLE 1

Properties of the soils used in the study, indicating also the region or important feature each represents and the background U concentrations.

Soil	Region or feature[1]	Texture[2]	Bkgd.U (mg/kg)	Clay (%)	CO_3[3]	CEC[4] (cmol /kg)	Organic matter (%)	Available P (mg/kg)
A	PH	L	2.1	24	a	14.4	2.2	5.0
lB	limed sand	fine S	0.6	2	a	11.0	1.0	17.0
G	garden	fine SL	3.1	18	vl	50.5	18.4	8.6
uB	acid sand	fine S	0.6	2	a	5.4	0.7	10.6
E	EL sand	LS	4.1	6	vl	17.0	3.5	1.6
X	PH medium	fine SL	2.1	15	vl	13.0	2.6	19.6
Y	PH light	L fine S	1.5	4	a	4.4	0.8	6.0
Z	PH organic	fine SL	1.8	13	a	19.9	5.7	40.6
#1	clay	CL	2.1	33	a	24.1	3.1	14.0
#2	carbonated	fine SL	2.1	12	l	17.8	4.2	9.6
#4	organic	O	4.9	<1	a	81.4	41.5	48.0

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[1] The regions are PH (Port Hope, Ontario) and EL (Elliot Lake, Ontario).

[2] Symbols denoting texture are C (clay), L (loam), O (organic) and S (sand).

[3] Carbonate content was qualitatively assessed, based on reaction to drops of HCl as: a (absent, typically <0.1% CO^3), vl (very low) and l (low, about 1% CO_3).

[4] CEC stands for cation exchange capacity.

The B soil was too acidic for many crops, but was important as a representative of boreal forest settings. Therefore, it was used both limed and unlimed, designated as lB and uB, respectively. The liming rate was determined by a 2-week incubation study, as well as previous experience with this soil. After application of 0.5 g $CaCO_3$/kg, the pH was raised to about 6.5. The edaphic variables listed in Table 1 were determined following standard procedures by the Manitoba Provincial Soil Testing Laboratory and the Saskatchewan Research Council.

Uranium Treatments, Replication and Statistical Analyses

The emphasis of this study was on U concentration levels found as extremes in the environment, but higher levels were included to ensure correct interpretation of symptoms and other effects. An optimized matrix of U levels and replication was used in each part of the study. The levels, as mg U/kg soil, and in brackets the number of replicates, were 0(4), 3(1), 10(2), 20(3), 30(3), 50(3), 100(2), 300(1) and 1000(1). This gave a total of 20 treatment/replicate units. This matrix was repeated for each crop and soil combination in each of the experiments.

Interpretation throughout was guided first by a segmented regression, which identified apparent toxicity thresholds, and then by analyses of variance using the general linear model (GLM) of SAS (1985). The segmented regression was iteratively fit so that at U levels below a threshold (TU), the response (Rs) was defined as a constant (C); and at U levels above TU, Rs was a decreasing linear function of U level with slope -b; as follows:

if $U < TU$, then $Rs = C$

if $U >= TU$, then $Rs = C - b(U - TU)$

Bounds were set to limit b to negative values. When a value of TU could not be resolved, the iterative process found b = 0 and/or TU beyond the range of our treatments. When a value of TU was resolved, it was an effective, unbiased indicator of a toxicity response pattern. Once this pattern was identified, tests of individual means, at levels beyond TU, versus controls were done as one-tailed, single-degree-of-freedom contrasts. The bounds on b and the use of one-tailed tests arises from rejecting hormesis as a valid hypothesis in this study.

The uranium was acquired as (natural, undepleted with respect to ^{235}U) uranium oxide powder and was dissolved in a minimal amount of concentrated nitric acid. In order to ensure that nitrogen (N) supply did not interfere with results, the N applied in each treatment below the 100 mg U/kg level was adjusted using NH_4NO_3 to the N level of the 100 mg U/kg treatment. As a result, treatments above the 100 mg U/kg level had more N than the lower treatments. It was inappropriate to elevate all treatments to very high, but uniform, N levels, as this would have been atypical of normal garden or agricultural settings.

Soil Range Experiment

All 11 soils were used in the soil range experiment, in order to examine the effect of edaphic factors on U toxicity. The soils included the A, 1B, and G soils used in the full maturity experiment (not reported here), the unlimed B soil (uB), soils representative of Elliot Lake (E) and

Port Hope (X, Y, Z), Ontario, and soils used by Sheppard et al. (1989) (#1, #2, #4) in a previous experiment with U (the uB soil was used by Sheppard et al. as their #3 soil). Aliquots of 450 mL of soil were placed in 1-L plastic containers. The U, nitrogen and lime were added, the soils thoroughly mixed and the soil transferred to 500-mL plastic containers. Bean seeds previously selected for weight uniformity were sown at 25 per container, 1 cm below the soil surface. The soils were wetted to 90% of field capacity, and the containers sealed and incubated at 20°C for 10 d. The numbers of germinated seeds were recorded.

Plant Species Experiment

This experiment measured germination of corn, lettuce, tomato, short-life-cycle *Brassica rapa* and white pine. The G and 1B soils were used, and 2.25-L aliquots were treated in 5-L plastic containers. These aliquots were then split into five, 500-mL plastic containers and the seeds sown. We sowed 25, 100, 100, 25 and 50 seeds per pot for each of the crops, respectively.

In addition to the treatment/replicate schedule used in the other experiments, we included several series of further treatments for the *B. rapa* only. The U treatments were increased to include duplicates of 300, 1000, 3000 and 10000 mg U/kg. Also included were two other series of duplicated treatments, one with 10, 20, 30, 50 and 100 mg As/kg and the other with 50, 100, 300, 600 and 1000 mg Zn/kg. The As was applied as solutions of $Na_2HAsO_4.7H_2O$ and the Zn as solutions of $ZnSO_4.7H_2O$.

Final emergence counts were recorded for all crops, and several intermediate counts were possible for the pine. The corn seedlings were retained and dry weights determined.

The pots containing *B. rapa* were thinned to six plants and the plants grown to maturity in the growth chamber. Effects of U on yield at maturity and on second generation seed germination will be available in later reports.

RESULTS AND DISCUSSION

The toxicity of U did not vary substantially among the soils of the soil range experiment, and there was no overall toxicity (Table 2). A few treatments had means significantly below the controls, but most of these did not conform to a smooth, continuous response curve as expected in a concentration series study. Given the probability level of $P=0.05$, a false conclusion rate of one-in-twenty statistical contrasts is expected, and this may account for these occasional, spurious indications of significance. There was a significantly lower germination in the #1 soil, and the regression analysis also showed a threshold level (at 530 mg U/kg) in this soil. Thus, toxicity was apparent in this soil. However, it is not clear why toxicity would have been more acute in this soil compared to the others. This soil is a high-pH, clay loam that strongly sorbs U (Sheppard et al. 1989). Perhaps even this result is attributable to the statistical error rate. There were several cases of decreased germination

TABLE 2

Germination (%) of bean in 11 soils as effected by U[1]

Soil	Control[2] (n=4)	Uranium treatment (mg U/kg) 10 (n=2)	20 (n=3)	100 (n=2)	300 (n=1)	1000 (n=1)
A	97 TU	96	96	96	88	92
1B	96 TU	98	96	96	96	92
G	76	82	79	60	80	96
uB	98 TU	94	99	98	100	92
E	98	96	99	96	92	100
X	74	70	69	92	92	48
Y	99	96	95	94	100	100
Z	93	74 *	93	98	96	100
#1	85 TU	74	95	84	88	48 *
#2	86	82	63 *	92	24 *	92
#4	90 TU	80	67 *	72 *	52 *	72

[1] Only controls and those U concentrations where at least one value was significantly different from the corresponding controls are shown. Significance relative to the controls (i.e. within each row) is indicated by * and is based on one-tailed, single-degree-of-freedom contrasts with $P<0.05$.

[2] Control values followed by 'TU' are of soils where segmented regression showed a threshold U concentration; beyond the threshold, germination percentages showed a decreasing trend.

in the #4 soil, but there was no decrease at 1000 mg/kg. This soil was organic and, because of the strong retention of U observed in organic soils, it is the most unlikely soil type in which toxicity might occur.

When crops other than beans were investigated, toxic effects were more apparent (Table 3). In the B soil, all crops had significantly reduced germination at 1000 mg U/kg, and threshold values were indicted by the regression analyses. The thresholds for corn, lettuce, tomato, *B. rapa* and white pine were 320, 300, 300, 0 and 11, respectively. The latter two threshold values are well below where significant decreases occurred. The tests of significance indicate actual thresholds for these crops at between 300 and 1000 mg U/kg, the same as for the other crops.

The G soil had more organic matter and a finer texture than the B soil and, therefore, less toxicity was expected. The results confirmed this; there were no systematic decreases in germination up to 1000 mg U/kg for any of the crops. Even when the concentrations were as high as 10000 mg U/kg for the *B. rapa*, there was no significant decrease. The regression analysis did show a threshold for the *B. rapa* at 750 mg U/kg, but this was not found to be significant by the tests.

TABLE 3

Germination (%) of five crops in two soils as effected by U[1]

Crop	Control[2] (n=4)	Uranium treatment (mg U/kg) 20 (n=3)	100 (n=2)	300 (n=1)	1000 (n=1,2)[3]	3000 (n=2)	10000 (n=2)
			limed Boreal soil (lB)				
corn	83 TU	87	80	88	52 *		
lettuce	62 TU	45 *	--[4]	78	7 *		
tomato	33 TU	44	60	93	7 *		
B. rapa	73 TU	67	76	71	26 *	2 *	0 *
pine	59 TU	48	32 *	66	0 *		
			garden soil (G)				
corn	87	89	90	84	100		
lettuce	87	72	89	55 *	91		
tomato	68	74	65	50	94		
B. rapa	68 TU	83	81	71	67	64	21
pine	54	66	36	66	66		

[1] Only controls and those U concentrations where at least one value was significantly different from the corresponding controls are shown. Significance relative to the controls (i.e. within each row) is indicated by * and is based on one-tailed, single-degree-of-freedom contrasts with $P<0.05$.

[2] Control values followed by 'TU' are of soils where segmented regression showed a threshold U concentration; beyond the threshold, germination percentages showed a decreasing trend.

[3] There were duplicates of *B. rapa* only at 1000 mg U/kg.

[4] Planting of this treatment was inadvertently missed.

These data indicate that, at least for germination, U is not very toxic. The concentrations of As and Zn that decreased germination to 50% were about 8- and 3-fold lower than that of U for the same effect (Figure 1). Significant toxic effects of U on seed germination were not evident at concentrations below 300 mg U/kg, well above levels found in most areas contaminated by industry. In those areas where levels of 300 mg/kg are found, it is very likely that other contaminants will pose more important hazards. Arsenic and several radionuclides are often found in concert with high levels of U. Despite these findings, it is important to base final recommendations on data from crops taken to full maturity, and these results are pending.

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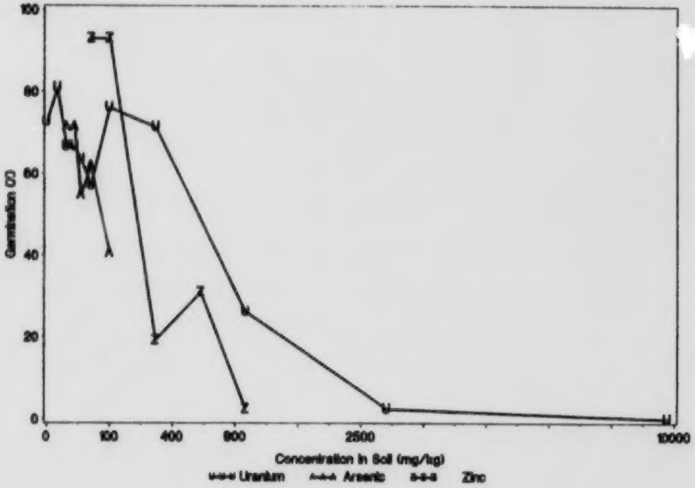
Figure 1. Germination of B. rapa as affected by uranium, arsenic and zinc in the Boreal (B) soil.



VOLUME I

SESSION A

AIR QUALITY RESEARCH

POSTER PRESENTATIONS

AP1

IDENTIFICATION OF ODOURS

THE CHALLENGE OF THE NINETIES

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Introduction

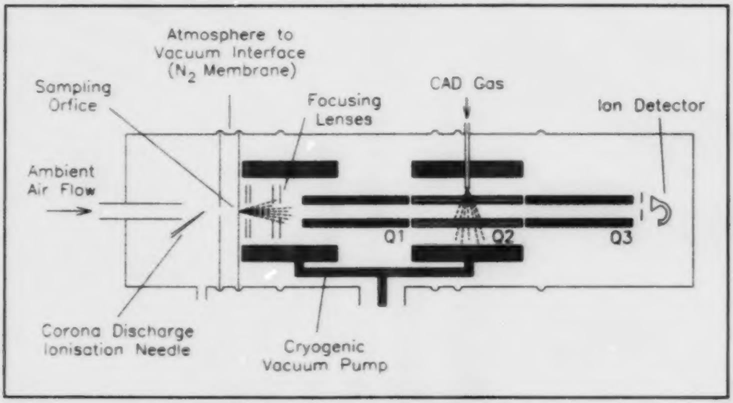
Odours, once tolerated, are now the root of many air pollution concerns. The chemical analysis of odours is one of the toughest challenges facing today's environmental scientists. Odorous compounds are generally reactive, present at trace levels, and sporadic. Consequently, techniques for odour monitoring must be capable of rapid analysis, extremely sensitive, and maintain sample integrity.

Traditional sampling, where discrete samples are collected on sorbent materials, and analysis techniques (GC/MS) are subject to chemical artifact formations, compound losses, and transformations, particularly when polar compounds are involved. An approach adopted by the Air Resources Branch is to utilize the Ministry's state-of-the-art mobile tandem mass spectrometer, TAGA 6000. Odours can be chemically characterized in a matter of minutes by advanced APCI/MS/MS techniques. "Unknown" compounds can be identified on-site through the MS/MS spectral library. The real time monitoring capabilities of the mobile TAGA 6000 provides for the determination of instantaneous levels of a variety of odorous pollutants.

The TAGA 6000 "Fingerprinting" Technique

The Trace Atmospheric Gas Analyzer (TAGA) is a tandem mass spectrometer (MS/MS) with an unique air sampling inlet system and ion source (see Figure 1). Ambient air is sampled directly at a high flow rate of 100 litres/minute into the ion source, which is operated at atmospheric pressure. Ionization of trace contaminants is achieved by chemical ionization (CI) initiated by a corona discharge. Selective ionization of chemical classes is achieved through the addition of an appropriate CI reagent to the flowing air sample. For example: atmospheric water vapour highlights ketones, aldehydes, alcohols, acids and ethers; oxygen highlights phenols, chlorophenols and acids; benzene highlights aromatic compounds and sulphurous species; and ammonia highlights amines, amides and nitrosoamines.

Figure 1: Schematic of the TAGA 6000 System.


Atmosphere to
Vacuum Interface
(N2 Membrane)
Sampling
Orfice
Focusing
Lenses
CAD Gas
Ion Detector
Ambient
Air Flow
Q1
Q2
Q3
Corona Discharge
Ionisation Needle
Cryogenic
Vacuum Pump

Ionization of odorous pollutants yields a mixture of parent ions which are immediately subjected to single MS analysis by the TAGA. Pollutants are then identified by MS/MS techniques. Parent ions selected by the first quadrupole (Q1) collide with argon gas in the second quadrupole (Q2, RF only) undergoing collision activated dissociation (CAD) to form daughter ions, which are analyzed by the third quadrupole (Q3). The fragmentation pattern, or daughter ions, is characteristic of the pollutant which produced the parent ion. The resultant daughter ion spectra are then compared to a standard CAD library and the pollutants are identified. The sampling and indentification routine is achieved in a matter of minutes.

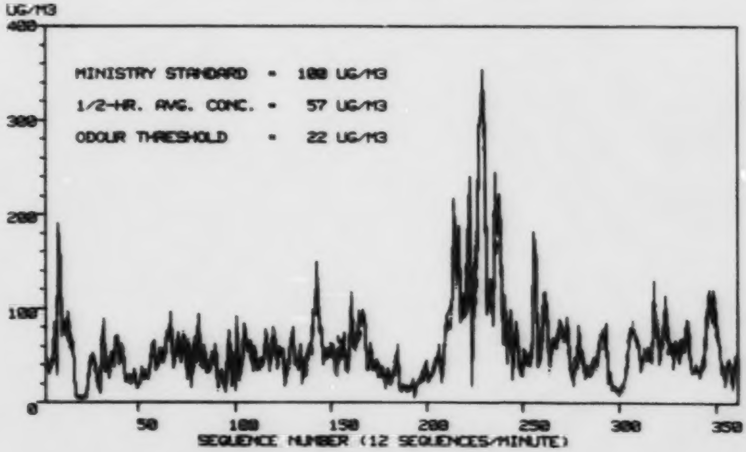
Quantitation of the Target Compounds

The target compounds are selected after determining a representative chemical fingerprint of the odours. Quantitation of a target compound is achieved by calibrating the response of the TAGA to known gas phase concentrations of the target compound. Typically, five-point calibrations are determined several times daily. Three parent/daughter ions are selected to monitor each target compound. The standard monitoring period for quantitative data is thirty minutes, with instantaneous measurements acquired every five seconds. A half-hour concentration is the average of 361 consecutive measurements. All monitoring data are correlated with meteorological information, which is recorded by the mobile TAGA unit.

Applications

The real time detection and the mobility of the TAGA 6000 allow the direct observation of short-term odour episodes (see Figure 2). For example, as shown in Figure 2, several instantaneous measurements of phenol exceeded the odour threshold limit, yet, the overall half-hour averaged concentration was below the Ministry Standard.

Figure 2: Instantaneous Phenol Levels Downwind of a Chemical Plant.



Another important capability of the Ministry's mobile TAGA 6000 is plume tracking, which is an integral part of the survey strategy. It provides unique information which is instrumental in source identification and monitoring site selection.

Summary

Over the last two years, the mobile TAGA 6000 has been applied to monitoring a broad range of volatile organic compounds, many of which have low odour thresholds; namely, acetates, amines, sulfides, phenols, PAHs, mercaptans, esters, ethers, acids, ketones, and aldehydes. Limits of detection are typically in the sub-ppb range. The ability to acquire meteorological data, in addition to the mobility of the TAGA unit, permits the tracking of source and fugitive emissions. Mobile monitoring has been effective in documenting short-term odour excursions, and fingerprinting a variety of odorous sources. The mobile TAGA technique allows real time data acquisition, providing temporal and spatial distribution of pollutants. This unit has been used to investigate the emissions from a variety of industrial sources including foundries, resin plants, incinerators, tar plants, painting operations, as well as, tire fires. Recent applications of the mobile TAGA 6000 to characterize odours will be presented.

AP2

CO_2 PRODUCTION AND CARBON CYCLING IN PRECAMBRIAN SHIELD WATERSHEDS

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Concern about increasing atmospheric CO_2 concentrations have stimulated research on carbon cycling in natural systems. Northern temperate forest watersheds cover a large part of northern Ontario and Canada and have recently become the focus of intensive research regarding nutrient cycling. To understand the effect of anthropogenic influences on their carbon cycle, such as acidification and climate change, the magnitude and pathways of carbon fluxes in these ecosystems must be evaluated. Generation of alkalinity which neutralizes acidic precipitation is also a part of the natural carbon cycle in watersheds.

Our research approach involves the use of isotopic (^{13}C, ^{14}C) and chemical tools to evaluate the carbon cycling in forested watersheds in the Precambrian Shield. Isotopic fractionation during carbon transfer among the different carbon pools, makes it possible to use carbon isotopes as natural tracers to evaluate sources and sinks of carbon and transfer rates between and residence times in the various carbon pools.

The overall objective of our research is to evaluate the carbon fluxes between the main carbon pools, atmospheric and soil CO_2, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), involved in the carbon cycle of these forested watersheds. Our research is comprised of two main aspects. a) The role of soil CO2 production in carbon fluxes and the generation of acid-neutralizing capacity in a subcatchment and b) carbon mass and carbon isotope balances in the lake watershed. These whole lake mass balance will then be used to estimate ; a) The net CO_2 flux from surface water to the atmosphere and the net conversion of inorganic carbon to organic carbon in the epilimnion; b) The conversion of organic carbon to DIC and DIC input from sediments porewaters in the hypolimnion zone and; c) The importance of the DOC and POC conversion to DIC in the lake DIC budget.

The study sites, Harp and Plastic Lakes, are located in the District of Muskoka, Ontario. These two lakes with differing physical characteristic, were selected as end members by the

Dorset Research Centre of the Ontario Ministry of the Environment as part of their research concerning the effects of acidic precipitation in lake ecosystems.

The first phase of this project has focussed on the evaluation of the carbon cycle of Harp Lake. Three representative subcatchment areas (Harp 4, Harp 5 and Harp 3A) of Harp Lake watershed are being monitored to characterize the watershed inflow to Harp Lake. Plastic Lake watershed will be more intensively studied during the second phase of this project.

Soil CO_2, groundwater, streams, and lake water are being extensively sampled for isotopic and chemical analyses to evaluate spatial and temporal variations of the main carbon pools and fluxes. The main parameters that are being measured are PCO_2, temperature, pH, DIC, DOC, POC and alkalinity. ^{13}C and ^{14}C analyses are performed on soil CO_2, DIC, DOC and POC samples. Mass spectrometry and tandem accelerator mass spectrometry are being used for ^{13}C and ^{14}C analyses respectively. The lake sampling is conducted in the deepest part of the lake and includes a detailed sampling of the epilimnion and hypolimnion waters.

The main observations of the data gathered during part of 1989 and 1990 can be summarized as follow:

Soil CO_2 profiles show higher CO_2 concentration during the summer months. Root respiration, oxidation of organic matter, and diffusion of CO_2 to the atmosphere are the main processes that control the production and distribution of soil CO_2 in the soil profile. ^{14}C analyses in soil CO_2 and soil organic matter will provide us with more information about CO_2 cycling.

The average $\delta^{13}C$ value for the soil CO_2 is around -22 o/oo. The groundwaters are characterized by an average $\delta^{13}C$ value of -23 o/oo. This is a clear indication that the main process responsible for the generation of alkalinity in this subcatchment is weathering of silicates. This is important in modelling the evolution of the groundwater chemistry from recharge to discharge areas. This also implies that ^{14}C can be used as a tracer to estimate the residence time of the groundwater in the basin.

Groundwater DIC in the higher part of the basin is characterized by ^{14}C activities in the range of 116 percent carbon modern (pmc) to 120 pmc. These values are close to the atmospheric CO_2 during 1990 recharge season. Lower ^{14}C activities (112 pmc) are observed in groundwater DIC in the discharge areas. This suggests that this groundwater was probably recharged into the aquifer at least 30 yr ago. Conversion of older DOC to DIC along the groundwater flow path could also be responsible for part of this pattern.

Stream DIC during spring time are characterized by a ^{13}C composition similar than the groundwater. However, a trend to more enriched $\delta^{13}C$ value is observed toward the end of the summer and fall. This pattern could be associated with isotopic exchange with atmospheric CO_2 and/or photosynthetic activity along the stream course. ^{14}C and PCO_2 data will provide more information to evaluate the importance of these processes.

$\delta^{13}C$ DIC profiles in the lake show a significant change in ^{13}C values from -20 o/oo to -8 o/oo in the epilimnitic waters from spring overturn to late summer. This isotopic pattern could be associated with photosynthesis and/or isotopic exchange with atmospheric CO_2. During photosynthesis, phytoplankton preferentially use the lighter carbon isotope (^{13}C) as a carbon source, leaving the residual DIC enriched in the heavy carbon isotope. Isotopic exchange with atmospheric CO_2 will change the DIC $\delta^{13}C$ signature in the same direction as photosynthesis. Since Harp Lake is in general oversaturated with respect to CO_2 and then a continuous source of CO_2 to the atmospheric CO_2 (P. Dillon, M.O.E, unpublished data), isotopic exchange should be a minor process. Preliminary ^{14}C data in lake DIC also support this statement.

The hypolimnetic DIC $\delta^{13}C$ show an opposite isotopic trend to the epilimnitic DIC. A change to more depleted $\delta^{13}C$ values from -20 o/o to almost -26 o/oo is observed toward the fall. This isotopic shift is due mainly to oxidation of organic matter falling through the water column. The average $\delta^{13}C$ for particulate organic carbon (POC) is in the order of -28 o/oo. However, the input of DIC from sediment pore water to the hypolimnion DIC cannot be ruled out. Although, preliminary measurements of DIC in surficial hypolimnetic sediment pore water, yield a $\delta^{13}C$ of -22 o/oo.

The effect of biological activity in the carbon cycling of the lake can also be observed in depth distributions of pH and DIC concentrations. pH increase in the epilimnion water from spring overturn toward the fall. The opposite is observed in the hypolimnion water. Hypolimnetic pH decreased during the same period. These patterns are the results of the redistribution of CO_2 (aq) in the water column due to photosynthesis in the epilimnion and remineralization in the hypolimnetic water and possible sediments.

DIC profiles show an opposite trend than pH profiles. For the period spring overturn to fall, they show a decreased in DIC concentration in the epilimnitic water and an increase in DIC concentration in the hypolimnetic water. The changes in DIC concentration are caused mainly by the same processes that change the pH distribution. Redistribution of CO_2 (aq) in the lake due to photosynthesis and remineralization of organic matter.

DOC cycling in groundwater, streams and lake water is being evaluated in a companion research project.

The lower DOC concentration are observed in the groundwater (~2 ppm). Higher concentration are found in the shallow part of the soil zone (LFH horizon) and in streams draining wetlands. These last areas are the major contributor of terrestrial DOC to the lake. DOC mass balances for Harp Lake indicated that this lake is net sink for DOC.

The hydrophobic fraction of DOC (humic and fulvic acids) and samples of total DOC have been processed for carbon isotope analyses.

Humics, fulvics and total DOC samples have a similar $\delta^{13}C$ range than their possible precursors, terrestrial C_3 plants and aquatic phytoplankton. ^{14}C data on DOC fractions show higher ^{14}C activities in the fulvic acid fraction compared to the humic fraction, indicating that aquatic humic substances are more refractory than the aquatic fulvic acids.

In general, surface water, including streams, wetlands and lakes contains a substantial amount of bomb ^{14}C, carbon incorporated into the global carbon cycle due to the input of ^{14}C from thermonuclear explosions after 1950. These high ^{14}C activities observed in DOC shows that cycling of a significant portion of this carbon pool in natural watersheds occurs on a short timescale (less than 40 years). This finding implies that the potential exists for anthropogenic activities, such as increase in acidic deposition, to alter the turnover rate of DOC which can have an effect in the acid-base chemistry of waters, and the mobility of metals and organic contaminants. The main results of the first phase of the research on DOC cycling in the Harp Lake watershed can be found in Schiff et al, 1990.

Preliminary sampling have also been carried out in Plastic Lake Watershed. This study site will be extensively investigated during the second phase of this project.

Schiff, S.L., Aravena, R., Trumbore, S.E and Dillon, P.J. 1990. Dissolved organic cycling in forested watersheds: A carbon isotope approach. Water Resources Research, in press.

AP3

MODELLING THE LONG RANGE TRANSPORT, TRANSFORMATION AND DEPOSITION OF MERCURY

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Over the last two decades information on the health effects of mercury, the buildup of methylmercury in fish in remote lakes and the role that atmospheric transport plays in the mercury cycle have increased considerably. Epidemics of methylmercury poisoning in Japan and Iran have identified the effects of methylmercury and have been used to establish dose response curves.

Although most severe mercury contamination problems due to local point sources have been eliminated, a more widespread concern about the buildup of methylmercury in predatory fish in remote lakes has developed over the past decade. In Ontario many small lakes have measured fish methylmercury values above the Ontario guideline. Indications from a number of studies suggests that the atmosphere is the primary source for the total mercury in remote lakes. Mierle (1990) examined a number of drainage basins in the Dorset, Ontario area and concluded that atmospheric loading coupled with the percentage of the drainage basin occupied by wetlands could account for observed total mercury levels in lakes. Methylation and bioaccumation processes would then play the key role in determining if these were a fish methylmercury problem for a given lake.

The most efficient means to delineate the atmospheric transport and deposition pathways is through numerical modelling. This paper presents a simplified atmospheric mercury chemistry scheme which has been implemented in an existing comprehensive Eulerian model framework (i.e. Misra et al. 1989, Venkatram et al. 1988). Some preliminary model results are discussed along with model enhancements currently being implemented.

Mercury Modelling

For this modelling effort, the mercury atmospheric system is assumed to consist primarily of 3 components: Hg°, particulate mercury and divalent mercury (i.e. $HgCl_2$ or HgO). These are the three main emitted mercury species and as indicated in Table 1 Hg° comprises > 95% of observed total mercury in the atmosphere. Of particular concern from a deposition viewpoint is the very different wet scavenging and dry deposition characteristics of these three species. Hg° is very insoluble and would thus be scavenged or dry deposited slowly (i.e. it has an estimated lifetime of several months in the atmosphere). On the other hand, HgII would be rapidly scavenged by rain and would readily dry deposit while nucleation scavenging by water droplets would efficiently remove particulate mercury. Even though observed air concentrations of HgII and particulate mercury are small they could form a significant fraction of the wet scavenged mercury and thus affect deposition patterns.

The modelling approach was to put a three species mercury system into an existing Eulerian model framework (i.e. Acid Deposition and Oxidant Model) using the best currently available emission inventory for eastern North America along with information on dry deposition rates, boundary conditions, and aqueous chemistry. The Eulerian model is modularised with sections dealing with transport and diffusion, dry deposition, mixing by clouds, scavenging within clouds followed by aqueous chemistry and wet deposition, and gas phase chemistry. The model domain encompasses eastern North America using a 33 x 33 grid with each cell 127 km by 127 km. The model includes 12 vertical layer distributed logarithmically to the 10 km level. Meteorological fields needed to run this model (i.e. winds, temperatures, stabilities, clouds, precipitation etc.) are derived in a preprocessing operation and put into the model as inputs. The other inputs needed are geophysical data such as terrain height and land use categories (percentage of grid: water, forest etc.) and emission rates for each grid square (or for individual point sources).

(a) Mercury Emissions

The anthropogenic emission inventory for mercury is dated and requires updating. Estimated total anthropogenic emissions are ~ 650 tonnes from the U.S. and ~ 31 tonnes from Canada. For the U.S. the important source categories were fossil fuel combustion at over 20%, use of paint and electrical equipment at 55%, non-ferrous metal smelters at ~10% and sewage sludge and municipal waste incineration at ~ 15%. The breakdown of Canadian emission was base metal recovery 45%, fuel combustion ~ 25% and paint volatilization ~ 15%. Preliminary model runs were performed by griding these emissions from state and province total emissions. In particular, the consumer goods part of the emissions was assumed to be related to population centres. In detail the distribution of these emission could be very different from that used. The use of mercury in paints as a fungicide agent would not necessarily be the same in different states.

Speciation of the emissions for initial model runs simply used a 90:5:5 ratio for Hg°: HgII : particulate mercury. A better breakdown of the emitted species is being prepared using sector speciation percentages suggested in Europe. For the North America emissions this leads to a 81:17:2 ratio for the mercury species.

Natural emissions of Hg° from soils or vegetation are poorly known. Model runs made use of emission factors over land which were a function of temperature (zero emissions below 0°C). Emissions from water surfaces were assumed to be zero. Over the eastern North America area, modelled natural emissions were similar in total to anthropogenic emissions. Although data is very limited a revised natural emission inventory is being produced.

(b) Gas phase mercury chemistry is poorly known at present. Given the low observed values of air HgII and particulate mercury concentrations, model runs have been performed assuming no net gas phase chemistry. This means that reduction reactions are assumed to nearly balance oxidation reactions. This assumption would affect the relative air concentration of the mercury species and therefore alter deposition patterns.

For aqueous phase chemistry the only reaction directly modelled is oxidation of Hg° by O_3 to give HgO. This reaction then allows more of the very insoluable Hg° to be adsorbed into water droplets. This mechanism was used in initial model runs.

More recent information suggests that other aqueous phase processes such as reduction by sulphate and adsorption of HgII or Hg° to particles in water also occur. Observations indicate that most of the mercury in precipitation ends up adsorbed on particles and that assumption will be used in future model runs.

(c) Dry deposition rates of Hg° should be small since the substance is very insoluble. Model runs to date have used a zero dry deposition velocity, however, more recent data suggests a small deposition to forests in the summer (i.e. ~ 0.03 cm s^{-1}) with little deposition to other surfaces or at other times. Further model runs will incorporate dry deposition of Hg° to forests. Even though the deposition rate is small the fact that air concentrations of Hg° comprise ~ 95% of the total mercury in air can result in significant dry deposition.

On the other hand, HgII species dry deposit very rapidly while particulate mercury is assumed to dry deposit at a rate similar to that for sulphate.

(d) The last important consideration for modelling the mercury system is the domain boundary values of the mercury species. Since Hg° molecules have a long lifetime in the atmosphere, boundary values of 1.5 ng m^{-3} at ground level are observed in remote areas. Particulate mercury concentrations of ~ 0.02 ng m^{-3} are also observed away from source regions. Model runs will make use of well mixed profiles for these compounds at all domain boundaries.

Model Results

Initial model runs were intended to provide only a magnitude comparison of modelled air and precipitation mercury concentrations with the very limited observed data (discontinuous air and precipitation readings at a few sites in North America). The model was run for a five day period in April 1981 for which meteorological data was already available. The last two days of these model runs produced the following results.

(1) Air concentration of Hg° were in the 1 to 3 ng m^{-3} range which is similar to the average observed values of 1½ to 4 ng m^{-3} away from source areas.

(2) Modelled air concentrations of HgII and particulate mercury were less than 0.05 ng m^{-3} using 5% of total emissions for each of these species. Very few reliable observations exist. Measured average particulate values in the New England area were ~ 0.06 ng m^{-3} while values in Wisconsin averaged ~ 0.02 ng m^{-3}.

(3) Concentrations of HgII and particulate mercury in precipitation varied strongly with precipitation amount which is consistent with rapidly scavenged species. For moderate precipitation areas both HgII and particulate mercury concentrations in precipitation were in the ½ to 4 ng l^{-1} range.

On the other hand, scavenging of Hg° produced only about 1 ng l^{-1} of mercury in precipitation.

The total modelled values of 3 to 7 ng l^{-1} is moderate precipitation is lower than the observed values of 10 to 20 ng l^{-1} but it must be kept in mind that the speciation of the emissions was very crude.

Future Work Plan

All aspects of the model formulations and the emission inventory are being updated as discussed above. Once this has been completed a series of sensitivity tests will be performed. Sensitivity test will be performed for some of the areas in which input data and model parameters are most uncertain. The sensitivity runs will be done for episodes of 5 to 10 days with the first 2 or 3 days used for model warm up.

1. Base Case Run.
2. 50% increase in anthropogenic emissions.
3. 100% increase in natural emissions.

4. Reduce anthropogenic HgII emissions and increase anthropogenic particulate emissions
   (a) 81% Hg°, 12% HGII, 7% particulate
   (b) 90% Hg°, 8% HGII, 2% particulate.

5. Dry deposition of Hg°:
   (a) Reduce the surface resistances to forests by a factor of 2 (i.e. deposition velocities closer to Lindbergs data).
   (b) Use surface resistances for cultivated levels etc. as twice the values for forests.

6. Final products of aqueous oxidation:
   Use 80% particulate mercury and 20% HgII as the species put into air when droplets evaporate.

7. Boundary conditions:
   (a) Reduce boundary values of Hg° by a factor of 2.
   (b) Reduce boundary values of particulate mercury by a factor of 2.

The University of Toronto has recently undertaken a 3 year project to model the cycling and bioaccumulation of mercury in remote Ontario lakes. To drive this modelling effort the loading of mercury deposited from the atmosphere is needed. As an adjunct to our current atmospheric modelling project long term gridded wet deposition of mercury will be produced using a simpler parameterization of the mercury system in a Lagrangian model. This will serve as a preliminary wet deposition field until the more detailed evaluation of the Eulerian mercury model has been completed. At that time an updated deposition field will be produced which reflects the knowledge gained in this project.

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Misra, P.K., Bloxam R., Fung C. and Wong S. (1989). Non-Linear Response of Wet Deposition to Emission Reduction: A Model Study. Atmospheric Environment 23, 671-687.

Venkatram A., Karmachandani P.K., and Misra P.K. (1988). Testing a Comprehensive Acid Deposition Model. Atmospheric Environment 22, 737-747.

Table 1 Typical continental background air concentrations of important atmospheric mercury forms and their respective Henry's law constants.

Compound	Concentration ng m^{-3}	Henry's law constant $H=[HgX]_g/[HgX]_{aq}$ (dimensionless)
Hg^0	2 - 4	0.3
$(CH_3)_2Hg$	0 - 0.01	0.3
CH_3HgCl	0 - 0.1	$1.5x10^{-5}$
$HgCl_2$	0 - 0.1	10^{-8}
particulate Hg	0 - 0.1	

AP4

ABSTRACT

An Investigation of Vibration Isolation in a House for Reduction of Train Vibration

Part 2: Characterization of Ground Vibrations from Trains

and

Part 3: Effectiveness of an Isolation System in Reducing Train-Induced Ground Vibrations

1. Background

The increased use of land beside railway lines for residential housing during the past decade has produced a rise in the number of complaints from nearby residents on the level of vibrations within their homes. These complaints have lead to a search for ways to isolate new homes from the effects of train-induced vibrations.

One method that appears promising is to place elastomeric pads between the ground and the superstructure. The method has been used successfully for many decades to isolate buildings from subway-induced ground vibrations and is now being recommended for residential structures near railway lines. However, the applicability of this method for different types of residential structures has not been tested nor has its effectiveness in reducing structural response to train-induced ground vibrations been demonstrated. Both aspects should be extensively examined from technical and financial viewpoints before elastomeric pads can be widely accepted as a satisfactory procedure for isolating residential construction. The goal of this three-part investigation was to provide some of this valuable information.

Part 1 of the investigation (Evaluation of Transducer Mounting in the Ground) was presented at the 1989 Technical Transfer Conference. Parts 2 and 3 are being presented at this year's conference. Part 2 (Characterization of Ground Vibrations from Trains) studied the frequency and propagation characteristics of train-induced ground vibrations at three sites in Southern Ontario. Part 3 investigated the effectiveness of an elastomeric pad system incorporated into a recently constructed two-storey row house. The residential structure was built within 50 m of a double-track rail line at one of the sites studied in Part 2.

2. Part 2 (Characterization of Ground Vibrations from Trains)

Frequency characteristics of ground-induced train vibrations were investigated at three sites located within the Ottawa-Montreal-Toronto triangle. The sites had substantially different surface profiles and soil conditions (soil type and depth). Track geometries at two of three sites were similar (track elevation at same level as adjoining land) as were track constructions (continuously welded rails supported on wood ties) and track number (double-track line). Rail traffic at each site contained both freight and passenger trains.

Ground vibrations were measured simultaneously at five stations along a measurement line perpendicular to the tracks with station distances ranging from 11 m (Station 1) to 160 m (Station 5) from the centreline of the tracks. Triaxial accelerations - vertical, transverse (perpendicular to the tracks) and longitudinal (parallel to the tracks) - were measured at Stations 1, 3 and 5 and vertical and transverse at Stations 2 and 4. Accelerometers were attached to the ground using the wooden mounting plate (175x175x19 mm) studied in Part 1 of the investigation.

One-third octave band analysis of vibrations produced by passenger and freight trains showed that site conditions were the most important factor affecting the frequency content and amplitudes of ground vibrations. Attenuation rates of one-third octave frequencies within the dominant frequency range were also site dependent. Although there was some indication of dependence of peak and broadband acceleration amplitudes on speed, type of train and train weight, the influence of site conditions greatly overshadowed any of these other variables.

The combination of a simplified site-dependent frequency spectrum near the track and a corresponding site-dependent attenuation rate is suggested as a design basis for vibration isolation systems of houses near railway tracks.

3. Part 3 (Effectiveness of an Isolation System in Reducing Train-Induced House Vibrations)

Part 3 examined the effectiveness of an elastomeric pad system in reducing the transmission of train-induced vibrations into a residential structure. The isolation system was placed between the superstructure and the top of the basement foundation walls in a two-storey residential row house. The house, a conventional wood-frame structure with a special precast concrete panel first-floor system, was within 50 m of a double-track railway line. The line was heavily used by commuter GO trains throughout the day. About 12 passenger trains and six freight trains also used the line on a daily basis.

House response to train passages was measured at four stations using accelerometers. Two stations were on the first floor slab and two directly below in the basement near the top of the concrete foundation wall. The accelerometers at each station on the first floor were paired by direction with the accelerometers in the basement. The pairing of station accelerometers was essential for the evaluation of the elastomeric pad system.

The measurements, taken before the installation of partition drywall, showed that

1) train-induced vibrations in the section of the house closest to the tracks were, over certain frequency ranges, smaller in the superstructure than in the foundation wall.

   The magnitude and frequency range of the reduction varied with direction; 3 to 9 dB from 40-80 Hz in the vertical direction, 4 to 10 dB from 50-125 Hz in the transverse direction (perpendicular to the track) and 4 to 16 dB from 25-125 Hz in the longitudinal direction. Outside these frequency ranges, vibrations in the superstructure were up to 10 dB larger than those on the foundation wall.

2) vertical vibrations in the section of the house farthest from the tracks generally exceeded those in the foundation wall throughout the 6-125 Hz frequency range.

   A possible reason for this behaviour was undetected material short-circuiting of the isolation system combined with low levels of train-induced vibrations in both the house and the ground at this location.

Because of the uncertainty in the effectiveness of this isolation system, additional studies of elastomeric pad systems should be undertaken.

AP5

SIMULTANEOUS REAL TIME DETECTION OF MERCURY AND HYDROGEN CHLORIDE IN AMBIENT AIR

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Introduction

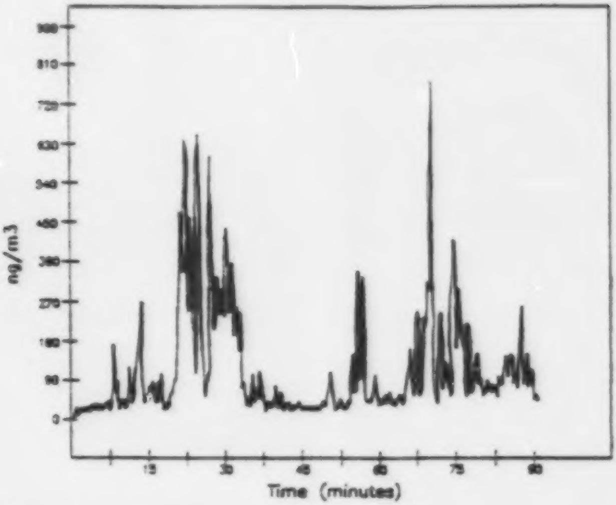
An incinerator plume may be located by simultaneously measuring, in real time, two of the plume constituents, namely mercury and HCl. A coincident elevation in ambient levels of both targeted pollutants can provide evidence that the pollutants originate from the same source. Chemical characterization of plumes via stationary monitoring devices is difficult given the capricious nature of local meteorology; however, by placing the monitoring devices in a mobile laboratory, the incinerator plume can be effectively tracked.

In this study, techniques were developed to concurrently measure trace levels of gaseous HCl and elemental mercury vapour in ambient air. HCl was measured using an atmospheric pressure chemical ionization (APCI) tandem mass spectrometer (TAGA 6000) while mercury was detected by a spectrophotometric method.

Mercury Analysis

Elemental mercury was monitored by a modified Scientrex HGP-2 mercury monitor because of its high sensitivity and real time response. Spectrophotometric analysis of mercury vapour was achieved by Zeeman absorption of the 254 nm mercury resonance line. Extensive work was performed prior to the survey to determine the detection limits and establish an appropriate QA/QC procedure. Detection limits were determined based on background measurements and were in the range of 10-15 ng/m^3 (2 ppt). Five-point calibrations, over a range of 0 - 500 ng/m^3, were performed to determine the linearity and consistency of instrument response. The data showed that it remained constant to within 5% over a period of 12 hours. Figure 1 is an example of some real time data for elemental mercury recorded by the Scintrex HGP-2 analyzer in an urban environment.

Figure 1: Real Time Data of Elemental Mercury.



Hydrogen Chloride Analysis

Since commercial HCl detectors lack the sensitivity for low ppb detection, a method was developed to monitor gaseous HCl via APCI/MS/MS. The ion chemistry under APCI conditions is dominated by dissociative attachment reactions:

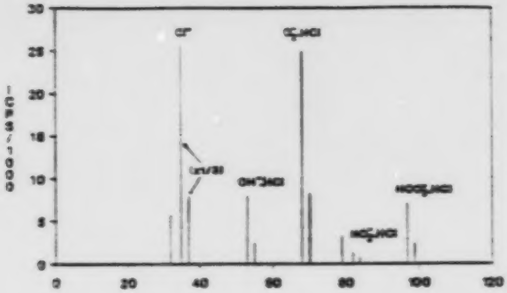
$$Y^- + HCl \rightarrow YH + Cl^-$$

where Y refers to OH, SO_2 or CO_3, and by reactions leading to the formation of adduct ions:

$$XY^- + HCl \rightarrow XY^- \cdot HCl$$

Where XY may be OH, O_2, NO_2 or HCO_3. A background-subtracted mass spectrum of HCl obtained by admitting trace amounts of HCl gas to the APCI source is shown in Figure 2. The anions at masses (M-1), (M+17), (M+32), (M+46) and (M+61) amu are produced by HCl deprotonation, and HCl clustering with OH^-, O_2^-, NO_2^- and HCO_3^-.

Figure 2: Single MS Spectrum of HCl



Since Cl^- ion may arise from a variety of Cl-containing compounds it is not a good identifier of HCl in the presence of other chlorinated species. It was found however, that selective monitoring of the cluster ion $O_2^- \cdot HCl$, and to a lesser extent $OH^- \cdot HCl$, together with the ability of MS/MS to separate the ^{35}Cl and ^{37}Cl isotopes, provides a reliable mechanism for identifying HCl in a complex matrix including other chlorinated compounds. The MS/MS daughter ion spectra of the cluster ion $O_2^- \cdot H^{35}Cl$ and $O_2^- \cdot H^{37}Cl$ is shown in Figure 3A and 3B. Note that the hydrated ion of O_2^- at 50 amu, shown in Figure 3A, is a daughter ion of double-hydrated ion of O_2^- at 68 amu. The limit of detection for HCl was approximately 0.5 μg/m³ (70 ppt). The linear detection range, determined by calibration, was 0 to approximately 60 μg/m³.

Figure 3A: Daughter Ion Spectrum of $O_2^- \cdot H^{35}Cl$

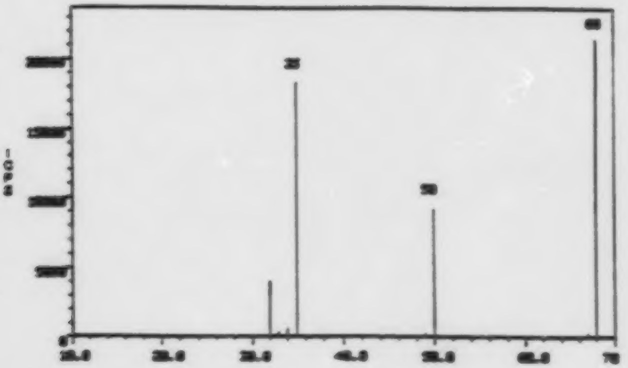
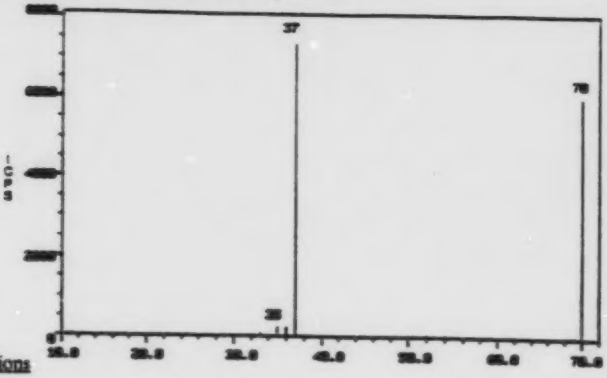


Figure 3B: Daughter Ion Spectrum of $O_2^{-} \cdot H^{37}Cl$



Applications

The determination of real time levels of elemental mercury and gaseous hydrogen chloride, in conjunction with a mobile TAGA unit, may provide unique information regarding the impact of incinerator emissions at the ground level. Potential sources of mercury and HCl include municipal waste and biomedical waste incinerators. This technique, which has been recently field tested, will be applied to ambient air studies in the future, where the simultaneous emission of HCl and Hg occurs.

AP8

A Residence Time Analysis of Air Data from the Acidic Precipitation in Ontario Study (APIOS)

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Ontario Ministry of the Environment,
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Introduction

Acid rain monitoring has been carried out by the Ontario Ministry of the Environment since 1980 under the auspices of the Acidic Precipitation in Ontario Study (APIOS). One of the objectives of the study has been to determine the major emission areas contributing to deposition of acidifying species to sensitive regions of the province.

Previous analyses combined meteorological and deposition data to characterise the contributions of the Sudbury smelters and the long range transported component to deposition in Ontario (e.g., Chan et al., 1982; Tang et al., 1986). The present analysis also uses the directional information contained in air parcel back trajectories, but goes further to extract information on distance to define the relevant source areas more precisely.

Experimental

The concentration data used in this study were obtained at Dorset, in the acid-sensitive Muskoka region of central Ontario. The main thrust of this work was aimed at concentrations in air, which were determined using a filter pack, with a 24 hour sampling period. Sulphate and nitrate were collected on a teflon filter, sulphur dioxide on a pair of cellulose filters impregnated with potassium carbonate in glycerol. In addition, some analyses were carried out on concentrations of sulphate and nitrate in precipitation. Precipitation samples were collected in a wet-only sampler (Aerochem-Metrics), also with a 24 hour sampling period. All samples were analysed by ion chromatography, after appropriate work up (Chan et al., 1985).

Residence Time Analysis Procedure

The residence time analysis procedure has been described by Poirot and Wishinski (1986). Briefly, air parcel back trajectories were calculated for each day for which a valid sample datum was obtained. The data, and the associated back trajectories, were then classified as high or low, by comparing the concentration with predetermined levels. These levels were chosen to be approximately equal to the 25th and 75th percentiles of the concentration of that species.

Eastern North America was overlaid with a 127 by 127 km grid, and each back trajectory was disaggregated so as to count the trajectory length falling within each grid square. This corresponds directly to the amount of time that the air parcel spent over the grid square. A geometrical correction was then applied to account for the fact that trajectories are more likely to pass over grid squares close to the receptor, and, in the limit, all pass over the home grid square.

The result of this analysis is an estimate of the relative amount of time spent over each grid square by air parcels corresponding to the observation of high or low concentrations at Dorset.

A sample of the results is given in Figure 1, which shows the residence time for air parcels associated with the observation of high concentrations of sulphate in air at Dorset. The contours contain respectively the areas within which the trajectories spent 25, 50 and 75% of their travel time for the specified conditions.

Results and Discussion

Air Concentrations

The main emphasis in this study was to apply residence time analysis to air concentrations of particulate sulphate and nitrate and gaseous sulphur dioxide. The analysis was confined to those days on which precipitation did not occur, since this reduced the perturbing effects of fronts and strong convective activity on the calculated back trajectories. The analysis was applied to a data set covering the years 1980 to 1985 inclusive, and was broken down by seasons.

The patterns for all three pollutants are similar. For high concentrations the trajectories spend most of their time to the southwest of Dorset, for low concentrations the isopleths lie in northern Ontario, and over Hudson Bay. The trajectories appear to be relatively short in the summer time, so that the 25% isopleth for high concentrations lies in southern Ontario and northern Ohio. In the winter this isopleth stretches much further to the south, and encompasses the Ohio Valley for sulphate and nitrate. The 75% isopleth is very similar for both seasons. For SO_2 the isopleths cover a smaller area than for sulphate or nitrate, particularly in the summer. This is consistent with the photochemical conversion of SO_2 to sulphate, which occurs more rapidly in the summer than in the winter.

Precipitation Concentrations

Although the calculated back trajectories are expected to be less accurate under precipitating conditions, the residence time analysis was also applied to high and low concentration categories of sulphate and nitrate in precipitation. These analyses were performed for all data, without a seasonal breakdown, and a sample is shown in Figure 2, which corresponds to the case of high sulphate concentrations. Again the difference between the patterns for high and low concentrations is very clear (high concentrations are associated with source areas to the south), while the behaviour for sulphate and nitrate is similar. These patterns indicate a significant westerly component, which is absent in the patterns for the air concentrations.

Overall

The residence time analysis very clearly implicates sources to the south, particularly including locations on the Ohio River Valley, as being associated with the observation of high concentrations of pollutants at Dorset. This observation applies to both air and precipitation concentrations. Conversely, low concentrations are associated with air parcels from the north. These results are consistent with a number of earlier analyses. The present analysis is unique in its ability to delineate the boundaries of the implied source areas.

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Poirot, R.L. and Wishinski, P.R. (1986) "Visibility, sulphate and air mass history associated with the summertime aerosol in northern Vermont", *Atmos. Environ.* 20,1457-1469.

Tang, A.J.S., Ahmed, A. and Lusis, M.A. (1986) "Summary: Some results from the APIOS atmospheric deposition monitoring program", Ministry of the Environment Report ARB-110-86.

Figure 1. High sulphate, summer

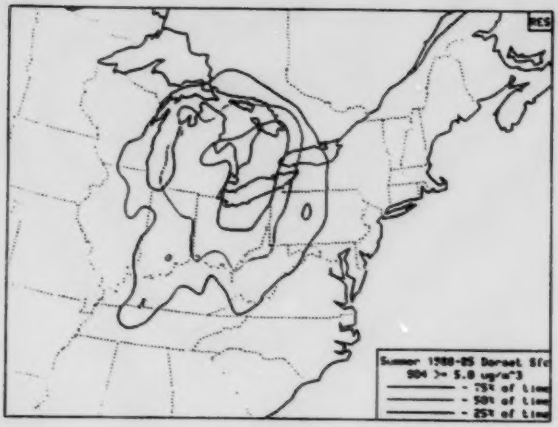
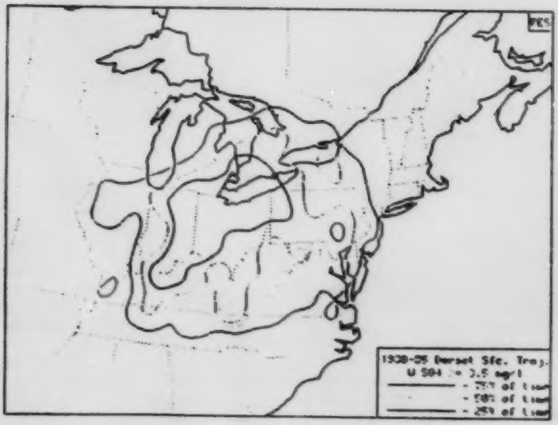

RES
Summer 1980-85 Dorset Sfc
SO4 >= 5.0 ug/m^3
- 75% of tim
- 50% of tim
- 25% of tim

Figure 2. High sulphate in precipitation


RES
1980-85 Dorset Sfc. Traj.
U SO4 >= 3.5 mg/l
- 75% of tim
- 50% of tim
- 25% of tim

AP7

MICROWAVE INDUCED CATALYTIC DECOMPOSITION OF SOME GASEOUS AIR POLLUTANTS

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INTRODUCTION

The deleterious effects on all living things of a variety of pollutants ubiquitous in the air, water and soil environments especially in industrialized countries have been recognized and extensively studied for several decades. Technologies for the reduction of additional sources of pollution as well as those directed at reversing or cleaning-up existing problems are the focus of much interest both academically and economically. In the areas of air pollution some of the principal concerns have been the effects of the acid gas pollutants SO_2 and NO_x, and the increasing changes effected by the vast volumes of CH_4 and CO_2 on the global weather patterns; the damage to the protective atmospheric ozone layer by hydrocarbon and halohydrocarbon effluents, and the carcinogenic and mutageic potentials of polyaromatic hydrocarbons and halogenated hydrocarbons.

This project involves the development and application of a novel technology which utilizes the selectivity and efficiency of mirowave interaction with different materials in order to facilitate the catalytic destruction of several airborne pollutants. The process has been named microwave induced catalysis and has been applied successfully to initiate and control a variety of chemical reactions of industrial significance including the conversion of methane to ethylene (1), the dehydrogenation of alkanes (2), and the oxidation of hydrocarbons using water (3).

The concept stems from the fact that different materials have an extremely wide range of abilities to absorb microwave radiation. Thus, most organic and many inorganic materials are poor absorbers of microwave and behave as though essentially transparent to incident microwave radiation. Other strongly absorbing materials such as many paramagnetic or ferromagnetic metals can concentrate and efficiently convert microwave radiation to heat. The catalytic technology utilizes this selectivity; the catalyst material consists of or contains the strongly absorbing "sensitizer" and is also chosen for its ability to facilitate the desired reaction, while the bulk of the reaction medium remains at ambient temperature and reactions occur primarily at the catalyst surface. Another particular advantage to microwave radiation as the reaction energy source is the ease with which it can be gated or pulsed. Appropriate pulse durations and periods allow control of reaction selectivity though control of the temperature of the catalyst surface; this also facilitates desorption of products from the surface and minimizes back reactions.

The general concept of microwave induced catalysis is applicable to a wide variety of reactions and the relative simplicity of the experimental design should allow modification to suit many industrial applications of environmental benefit. Indeed this concept has been described as an "enabling technology" whose applications have much wider significance than can be presented here. This report will briefly describe the application of this technology to the destruction of SO_2 and NO_x by reduction rather than conventional oxidative methods, and the dehalogenation of both aromatic and aliphatic hydrocarbons. Other applications to conversion of methane and CO_2 are also under consideration.

EXPERIMENTAL

The experimental methods and procedures for microwave catalysis reactions are a continually evolving process and there is no one general apparatus suitable for all applications; rather the optimal apparatus depends on the chemical system to be investigated. Early experiments to test the viability of the technique were illustrated using a simple commercial microwave oven modified to contain a pyrex reactor and connected to a vacuum line for injection of gaseous reagents; direct GC or GC/mass spectrometric detection is readily incorporated (Figure 1a). Subsequently a 3 kW variable Cober magnetron was used as the power source with appropriate microwave and electronic hardware to allow monitoring of the power absorbed or reflected by the reactor (Figure 1b). This design using millisecond pulses of kW power produced significantly improved conversions with much greater product selectivity compared to the microwave oven set-up in which powers of 250-400 W were produced and pulse durations of 2 - 10 s were typical. Further details of the experimental parameters are discussed elsewhere (4,5). Typically in experiments with either the acid gases or the halogenated compounds the reagents were flowed into the catalyst bed diluted in an inert gas and in concentrations ranging from 5 - 50 % until the catalyst bed was saturated. Microwave irradiation was then initiated while further reagent flow was continued. GC analysis was done on a Hewlett-Packard (Model 5890A) GC with either TCD or FI detection as appropriate. Commercially available supported catalysts including Ni-1404, Ni-1600, Cu-1700, Cu-1132, Ti-0404 from Harshaw/Filtrol Partnership, C-12 CO conversion catalysts from Chemetron-Girdler, C101-V_2O_5 from Catalyst and Chemicals, and Ni, Fe, Cu, graphite and CuO powders were used as well as some in-house catalyst pellets. For certain of the experiments initial activation of the catalyst under H_2 (30 kPa) while irradiating with ten 5 s pulses of 400 W average microwave power was performed.

RESULTS AND DISCUSSION

SO_2 and NO

Our aim in experiments with either of these acid gas reagents was to effect reduction of the starting material with the resulting production of O_2 and either S or N_2. In both cases it was possible to remove >99 % of the acid gas reagent with the corresponding production of O_2 as shown in (Figures 2,3), although in the SO_2 experiments only the total S produced was measured and the S containing product has not yet been speciated; it is however, adsorbed on the catalyst. Further experiments to elucidate aspects of the reaction mechanism using ethylene as a scavenger are underway.

In experiments with NO at long reaction times some N_2O was produced as well as N_2 and O_2. The appearance of this product indicated the oxidation of the catalyst surface; this could be dramatically hindered (i.e. irradiation time before catalyst oxidation increased by more than an order of magnitude) by mixing a coreductant (~10 % by volume) such as CH_4, H_2, or CO in the reagent gas stream.

Regeneration of the catalysts used by microwave irradiation under H_2 allowing repeated reuse of the catalyst material was readily accomplished.

Dehalogenation of Aliphatic and Aromatic Hydrocarbons

Halogenated and polyhalogenated compounds which are of environmental concern exhibit a variety of different structural features; a few model systems have been studied to demonstrate the potential of microwave induced decomposition towards these pollutants. These include methyl chloride, methyl bromide, dichloromethane, several chlorobenzenes, and triphenylmethyl chloride and bromide. In each case the catalyst bed was presaturated with the reagent of interest (15 -50 % in He) and the gas phase recirculated over the catalyst bed for the duration of the reaction. In each system the halogenated reagent was decomposed: for methyl chloride the only products detected were methane and dimethyl ether, whereas methyl bromide irradiation resulted in the formation of methane, methanol and dimethyl ether. Results for the dichloromethane and chlorobenzene decompositions are shown in Figures 4 and 5. In all cases substantial concentrations of chlorine were detected by elemental analysis of the catalyst material. As can be seen in Figure 4 dichloromethane dehalogenation appears to occur in a stepwise fashion with methyl chloride being formed as a reaction intermediate. Chlorobenzene was slightly more difficult to remove completely; 3.9 s microwave pulses reduced its concentration by ~60% with formation of benzene, CO_2, water and methane, while longer pulse durations effectively completely removed the starting material and also decomposed the benzene product to the less toxic products water, CO_2 and methane. Mechanisms for such surface catalysed reactions are very difficult to prove, however, the stepwise dechlorination of dichloromethane and the products formed in all the systems are consistent with free radical mechanisms. Furthermore, the microwave induced dehalogenation of either triphenylmethyl chloride or bromide over Fe or Ni powder in benzene produced a solution exhibiting the Electron Spin Resonance spectrum of the stable triphenylmethyl radical.

CONCLUSION

Microwave induced catalysis is a very versatile, fast, and energy efficient process which through suitable catalyst selection can readily be applied to the destruction or removal of substantial concentrations of gaseous or liquid pollutants. The microwave hardware components are commercially available and can be modified for a variety of applications. Ongoing experiments using this technology are directed at conversion of CO_2 to carbon and O_2, and methane conversions as well as the design and assessment of a higher power, shorter duration (megawatt / microsecond) microwave reactor for the processing.

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3. J.K.S Wan, M.Y. Tse and M.C. Depew, U.S. Patent Pending; M.Y. Tse, Ph. D. Thesis, November, 1990.
4. J. Wan, M. Tse, H. Husby and M. Depew, J. Microwave Power and Electromagnetic Energy, 25 (1990) 19.
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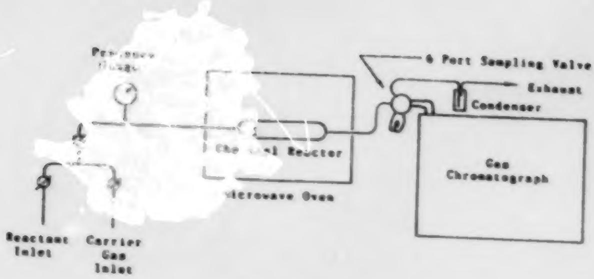
Pressure Gauge
6 Port Sampling Valve
Exhaust
Condenser
Chemical Reactor
Gas Chromatograph
Microwave Oven
Reactant Inlet
Carrier Gas Inlet

Figure 1a A Schematic Diagram of the Flow-Through Microwave Oven Reactor.

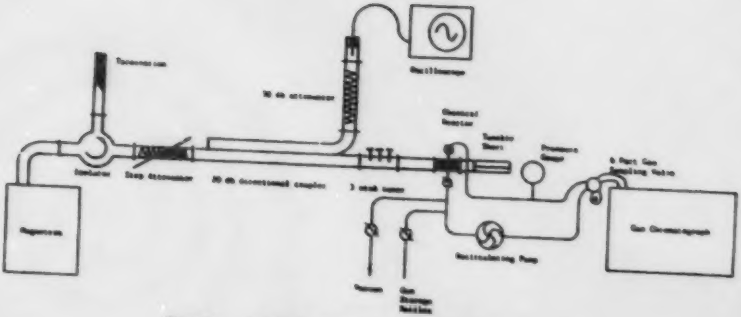
Termination
Oscilloscope
30 db attenuator
Chemical Reactor
Tunable Short
Pressure Gauge
6 Port Gas Sampling Valve
Isolator
Step Attenuator
20 db directional coupler
3 stub tuner
Magnetron
Gas Chromatograph
Recirculating Pump
Vacuum
Gas Storage Bottles

Figure 1b A Schematic Diagram of the Microwave Waveguide Reactor System: The Recirculating Flow Reactor

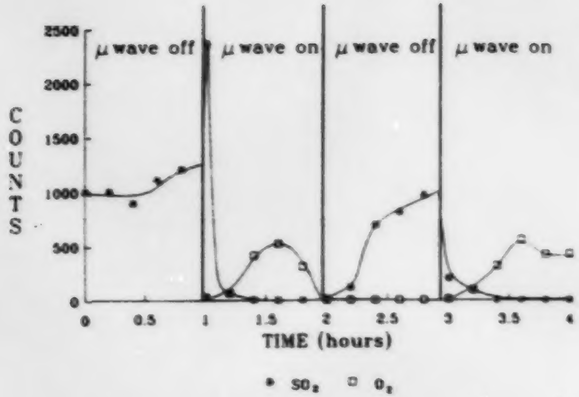

Figure 2 Decomposition of SO_2 Over Nickel/Nickel Oxide Catalyst (Harshaw Ni-1404)

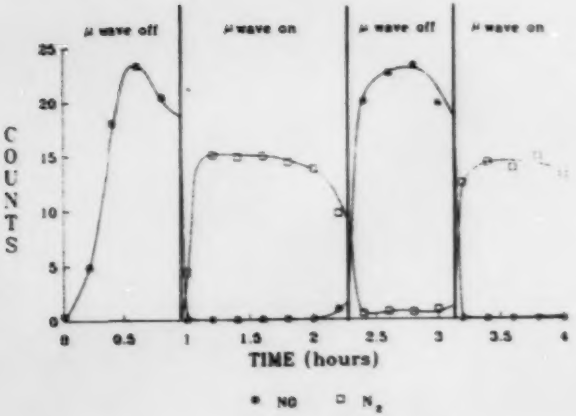

Figure 3 Decomposition of NO Over Iron Oxide Catalyst (Girdler C-12)

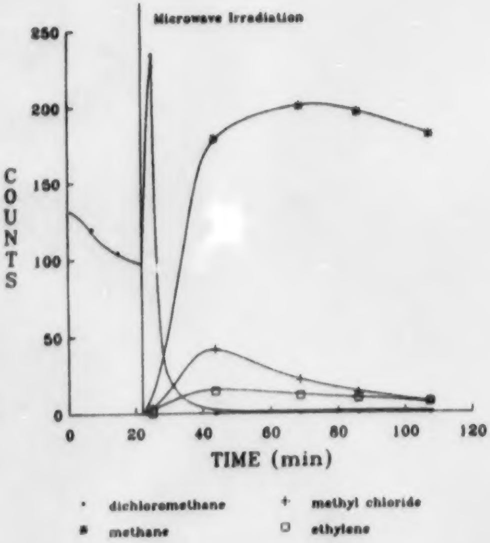

Figure 4. Decomposition of Dichloromethane in the Recirculating Microwave Oven Reactor

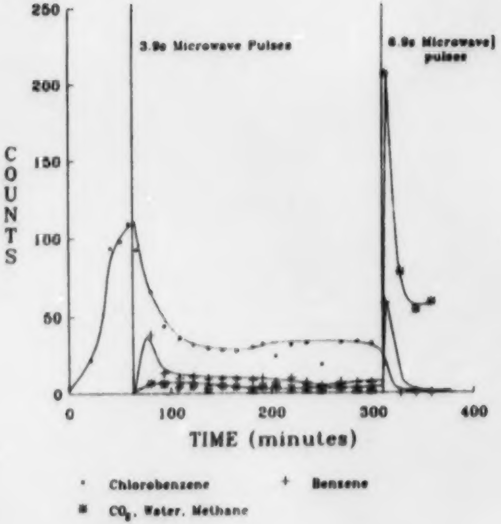

Figure 5 Decomposition of Chlorobenzene Over Nickel/Nickel Oxide Catalyst (Harshaw Ni-1404)

AP8

MESOSCALE AND LONG RANGE TRANSPORT MODELS ARE COMBINED TO MODEL POLLUTANTS ORIGINATING FROM LOCAL AND DISTANT SOURCES.

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1. INTRODUCTION

A mesoscale meteorological model 'GESIMA' is combined in this study with the Acid Deposition and Oxidant Model, ADOM. The two models will form a nested grid model allowing simulations of transport, chemical transformations and deposition of atmospheric pollutants with horizontal resolution of 20 km, as compared with the 127 km resolution of ADOM alone. Such a model can then be used to evaluate the impacts of various abatement strategies of the emissions of the precursors, nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in urban areas of Southern Ontario, for the control of ozone and other oxidants, or the impacts of variable controls of SO_2 and NO_x emissions for the control of acid deposition.

The ADOM model does not generate its own meteorological fields, using instead the 3-D fields of wind, temperature, humidity, and other meteorological parameters produced by a large scale NWP model of the Canadian Meteorological Centre (CMC). The high resolution simulations with ADOM are made possible by replacing those fields with 3-D meteorological fields generated by the mesoscale model.

The full run of the combined, nested model will consist of:

a. The 'regular', large scale run of ADOM using the meteorological fields taken from the output of the CMC model.

b. The high resolution run of GESIMA in the area of particular interest. The initial and boundary conditions will be derived from the CMC output.

c. The high resolution run of ADOM using the 3-D meteorological fields generated in step b. and the initial and boundary conditions derived from the results of the step a.

In this project the simulations are planned for two areas of Southern Ontario. Each domain will consist of 9 cells of the 127 km CMC grid of ADOM, with the Toronto cell in the centre of the first domain and the Windsor cell in the second one. In future, the area of simulations could be extended to the entire high ozone corridor extending from Windsor to Quebec City.

Two periods for which detailed air quality and emission data are available will be simulated, namely April 21 - 24, 1981 (the OSCAR IV period) and a high ozone episode of August 2 - 5, 1988. The results of the nested grid model will be compared with those of the 'regular' ADOM and with the observational data. The simulation will be carried out on the CRAY X-MP computer of the Ontario Centre for Large Scale Computation.

The project started in July 1990. The tasks completed to date (September 1990) concerned mostly modifications of GESIMA to allow its coupling with ADOM and assembling the data necessary for its run. The following sections describe those data, provide some background information and describe the recent modifications of GESIMA.

2. BACKGROUND

2.1 ADOM

The ADOM (Acid Deposition and Oxidant Model, sometimes also referred to as 'TADAP') is a comprehensive, sophisticated Eulerian model simulating the regional scale transport, chemistry and both 'wet' and 'dry' deposition of various atmospheric pollutants. The model has been developed by the ERT and MEP companies under the sponsorship of the Ontario Ministry of the Environment, Environment Canada, Umweltbundesamt (Germany), and Electrical Power Research Institute (USA). For details see Venkatram et al. (1988).

For the Canadian applications, the model is usually run using the '127 km' CMC grid (which actual size in the Toronto area is about 115 km) and the 3-D meteorological fields generated by the CMC NWP model. The model has 12 vertical layers, extending to 10 km and ranging in thickness from 56 m at the ground to about 2500m at the upper boundary.

2.2 GESIMA

GESIMA (GEesthacht SImulation Model of the Atmosphere) is a sophisticated, mesoscale model developed at the GKSS Forschungszentrum in Geesthacht, Germany. The model solves the non-hydrostatic, anelastic equations of motion in terrain-following coordinates using a predictor-corrector scheme. The dynamic pressure is computed using a conjugated gradients method (Kapitza and Eppel, 1987). The detailed description of the dynamics and numerics of the model is given by Kapitza, (1987). The turbulent diffusion is parameterised according to the mixing length approach. A sophisticated surface layer module is used for computing the heat and moisture balance at the ground level, taking into account the shortwave and longwave radiation, heat and moisture fluxes in soil etc. The model includes also a cloud module computing mixing ratios of cloud water, rain and cloud ice/snow (combined in one variable) using the 'bulk microphysics' approach.

The original GESIMA does not yet have any 'nesting' subroutines providing time dependent boundary conditions derived from an outer model, so all the initialisation and boundary condition procedures involving data from the CMC model had to be written specially for this study.

2.3 The 1989 Project

The adaptation of GESIMA aimed at its coupling with ADOM began in 1989. In the previous project (Niewiadomski, 1989, 1990) the GESIMA simulations were performed in the Toronto area, with the horizontal resolution of 5 km. The domain covered one cell of the CMC grid, with Toronto in its SW quarter. A test run of GESIMA covering the first day of the OSCAR IV period has been completed.

Since this project concerns much larger domain (9 CMC cells, approximately 345km x 345km, with horizontal resolution of 20 km as compared to one cell with 5 km resolution), the results of the last year run cannot be used to drive ADOM, so the GESIMA run must be repeated.

Although most of the modifications of GESIMA introduced during the 1989 project could be transferred to the new, improved version of the model received from Germany for this study, some initialisation and boundary condition schemes had to be completely rewritten for this project, due to the much larger domain.

3. MODIFICATION OF GESIMA

The comprehensive description of the GESIMA modifications is provided in the report of the last year project (Niewiadomski 1990). Only the vertical structure of the model and the changes specific to this study are briefly discussed below.

3.1 Initialisation

The original model is initialised with horizontally uniform profiles of all parameters. A similar procedure was adopted last year, when GESIMA ran in one cell of CMC grid and could be initialised with uniform profiles derived from the CMC model output. In this study, profiles from 9 CMC cells are available, so different parts of the domain will be initialised with different profiles. To avoid potential numerical instability resulting from horizontal discontinuities of meteorological parameters, and allow their smoother adjustment, the initial period of simulations may require a reduced time step. A similar initialisation procedure is planned (but has not been tested yet) for the mesoscale run of ADOM.

3.2 Time Dependent Boundary Conditions

The output of the CMC NWP model is available for each cell of CMC grid with time resolution of 1 hr. These profiles are used to determine the inflow boundary condition for each of four lateral boundaries of the GESIMA domain. First the hourly CMC profiles are interpolated in space, using values from 8 neighbouring CMC cells for each lateral boundary. At each time step of simulation, the inflow boundary values are then interpolated in time for each GESIMA using boundary parameters from the previous full hour and the following one.

A similar procedure is planned for the mesoscale ADOM simulation, with the pollutant fields generated in the large scale ADOM run replacing the meteorological fields from the CMC NWP model.

4. DATA ASSEMBLING AND PROCESSING

In preparation for the GESIMA run, several databases had to be obtained. The data for the particular domain and time period must be extracted from those databases and rewritten in a format acceptable by GESIMA. Most of the data obtained this way will also be used for the mesoscale ADOM run. The software developed for this purpose does not depend on the choice of particular domain, simulation period or horizontal resolution of mesoscale models and will be used in future runs of the nested modelling system. The data bases obtained and the preprocessing software are briefly described below. At the time of writing, the processing of air quality and emissions data necessary for the runs and evaluation of ADOM have not yet begun.

4.1 Meteorological Data

The meteorological fields generated by the CMC NWP model were obtained from the O.M.E. in the form of the input datasets for the 'regular' run of ADOM. Each dataset contains data for the whole ADOM domain, but only one level, so the preprocessing involves mostly the extracting data for the specified mesoscale domain and combining different levels in one profile for each cell. For each mesoscale domain of 3 x 3 CMC grid cells total of 25 hourly profiles of each parameter are needed, since data from the CMC cells adjacent to the mesoscale domain are used to determine boundary conditions.

4.2 Land Use

Land use information is needed in the surface layer submodels of both GESIMA and ADOM to determine surface parameters like albedo, heat capacity, roughness length etc. The data come form an E.P.A. database containing percentages of coverage of a given grid cell by 11 land use categories. The resolution of the EPA grid is similar to that of the mesoscale model but, since the both grids are not identical, the land use data for each mesoscale grid cell have to be interpolated from several (from 1 to 4) cells of the E.P.A. grid.

4.3 Topography

Both GESIMA and ADOM use terrain following vertical coordinates. The topographical data in form of contours in UTM coordinates come from digitised 1:250000 map tapes obtained from the Canada Centre of Mapping of the Energy Mines and Resources Canada. The processing of those data involves extracting the contours from other information, significant reduction of data (since the resolution of 1:250000 maps is much higher than that of the mesoscale model) and converting the contours to average elevations of each mesoscale grid cell. At the time of writing these tasks were well advanced but not yet completed.

5. CONCLUSION

Coupled GESIMA and ADOM models will form a nested mesoscale model capable of simulation of transport, chemical transformations and deposition of atmospheric pollutants with resolution of 20 km or less. The meteorological model GESIMA has been modified to allow its interfacing with ADOM. The necessary data have been assembled and are being preprocessed. The Toronto area run of GESIMA is expected to be completed in the fall 1990. The Toronto runs of ADOM and the runs of both models for the Windsor area will follow. In the future, the area of simulation could cover the entire Windsor- Quebec City corridor.

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AP9

RELATIONSHIP OF SUGAR MAPLE DECLINE AND CORRESPONDING CHEMICAL CHANGES IN SAP CARBOHYDRATES AND TRACE ELEMENTS

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INTRODUCTION

A systematic chemical information about the sap composition of sugar maple trees, both healthy and declining, is not available in the literature and is not covered by other studies in this field of sugar maple decline research. It is expected that if environmental factors have interfered with the biological processes of a normal maple tree, they would react with the biological and physiological composition of xylem sap carbohydrates, micronutrients and trace elements. The latter would perhaps be reflected in the major chemical components of the xylem sap and stem tissue. Five sample plots, previously established by OMOE as part of its Hardwood Decline Survey Project in 1986, were chosen for site studies. Early (March) and late (April) season sap were collected aseptically from these sites in 1988 and from two of these sites in 1989, and three other sites in 1990. Micro-, macro-elements and trace metals are analysed by AA and ICAP Spectroscopic methods. Mono-, di-, and oligo-saccharides in the sap were investigated by High Pressure Ion Exchange Chromatography (Dionex Corp., Sunnyvale, California). This method of sugar analyses offered a very high resolution (30-100 ppb) for quantitative chemical determination. The method was standardized in our laboratory and provides highly reproducible results. This method has eliminated the uncertainties associated with other existing methods of carbohydrate determination. To provide secondary support for the carbohydrate determination, various other biochemical parameters such as pH, dry weight, and refractive indices of the samples have been recorded for gross estimation. Compilation of data of all these response variables might provide an indication of biological disturbances and corresponding chemical changes taking place in declining maple trees when compared with healthy trees. Work on stem and soil matrices of these trees is also underway as part of a separate study.

We had earlier proposed that at the present stage of our scant knowledge of sugar maple decline, a useful approach might be to study the chemical changes occurring in sap in trees ranging from healthy to declined. The long-term objective being that if we could index the chemical change in xylem sap of declining maple trees, relationships could then be correlated with a physical assessment criterion, Decline Index (DI), recently formulated by OMOE and is currently being used in many related studies. It might further be possible to index these trees chemically much earlier than the onset of the physical decline, thereby facilitating the "early warning" syndrome of maple decline. The focus of this research, therefore, lies in chemical analysis of xylem sap. To the best of our knowledge, this scientific study has not yet been pursued by any other research group involved in sugar maple decline research.

EXPERIMENTAL DESIGN

The sampling unit of this study is an individual (healthy/declining) tree of any of the five sites selected in a NE to SW directional gradient of southern Ontario. Ten sugar maple trees, differing in physical health (as determined by OMOE's DI) and site characteristics (mainly pedological and stand) are selected each from five sites varying in their overall decline status. These sites were mapped out in 1986 as part of the Hardwood Decline Survey, conducted by MOE.

One of these sites has been demarcated as a "base-line site", which will provide a statistically acceptable pattern of variability in levels of sap chemicals. Fifty trees at various stages of decline have been marked for study at this site. This site will further provide data to study the extent of intra-site variability in these trees. All sites selected have been unmanaged for at least the past 17 years, contain at least 50% sugar maple trees, and are situated on the Crown Land, undisturbed by any man-made disturbances. The crossed factorial design of this study includes five sites. Some of the characteristic features and the site DI of these sites are shown in Table 1. Trees were selected so that the healthy trees have DI of <10.00 and declining trees are branded DI of >10 and <90.

TABLE 1

Site Number	Location	Decline Status	DI	Soil Type
AO62	Bancroft 45°20'/78°5'	Healthy	<12.5	Podzolic
AO61	Bancroft 44°50'/78°10'	Severely Declining	>17.5	Podzolic
AO73	Peterborough 44°20'/77°56'	Healthy	<12.5	Calcareous
AO45	Milton 43°32'/80°5'	Severely Declining	>17.5	Calcareous
AO20	Shelbourne 44°5'/80°28'	Moderately Declining	12.6-17.5	Calcareous

Within each category, an attempt was made to include some dominant and some suppressed trees to study the nature and effect of the stand competition on decline.

The present general trend analyses were performed on the basis of these decline categories rather than on the individual numerical values of the physical decline.

Xylem sap at breast heights (1.3 meters) of selected trees have been collected at both early and late sap flow seasons in March and April months of 1988, 1989 and 1990, respectively.

SAP COLLECTION

For sap collection, aseptic conditions were used to avoid metal contamination which might interfere with the trace elemental analyses. A custom designed polyethylene plastic suction apparatus was designed for the extraction of xylem sap in maple trees in the field by MOE. This apparatus was used for the extraction of sap samples in these sites. A two inch hole was drilled by an automatic drill attached onto a chain saw at the south side of the breast height of the trees. A maximum pressure of 120 psi, applied by hand-held lysimeter pump, was enough to yield sufficient sap (30-100) from each tree in 5-20 minutes. As mentioned in the abstract all 90 trees were tapped for sap samples twice during the sap season of 1988 and during 1989, four sap samples were taken from the ten trees of site 45 at weekly intervels and two samples each from ten trees of site 73 were taken at early and late season.

In 1988, a total of 180 sap samples were collected (90 early sap season samples and 90 late season samples from 90 trees). In 1989, 60 more samples were collected (10 each week from site 45 trees for four weeks and 10 early and late samples from site 73 trees). Forty sap samples were collected in 1990. The total volume of collected samples varied between 25-100 mL. Each extracted sap sample was aliquoted and distributed equally in 4 sterile plastic vials (30 mL capacity). The samples were kept cold in the field and frozen at -15°C as soon as possible. The frozen samples were thawed and diluted with deionized water prior to analyses.

ANALYTICAL PROCEDURES

Analyses of Carbohydrates and their derivatives.

Simple sugars and di- and oligo-saccarides were analysed by High Pressure Liquid Ion Exchange Chromatography (HPLIC), a new technique marketed recently by Dionex Corporation (Sunnyvale, California), as BioLC Series 4000i. This is a new chromatographic analysis method utilizing anion exchange separation of carbohydrates with pulsed amperometric detection. Compared to older chromatographic methods with refractive index and ultraviolet detection, anion exchange with pulsed amperometric detection provides specificity, selectivity, sensitivity and reliability. In our laboratory, the chromatograph has been interfaced with a Shimadzu CR5A integrator (Shimadzu Corp., Japan). Sugars in sap were identified and quantified against known standards.

RESULTS

Carbohydrates

Comparison of major pentosans, hexosans and sucrose were undertaken to estimate the relationship of sugar content in sap and degree of decline in maple trees. The experiments were done for both early and late sap samples.

Total Solid Content

Total solids in early and late sap were measured and refractive indices determined by RI measurements to establish the loss of mass.

pH of the Sap

pH of the early and late sap was measured to establish the chemical changes in the sap due to decline and time.

Micro and Macro Nutrients of the Sap

Most of the elements have been analysed by the ICP method. Sodium and Potassium have been analysed by the AA method.

Work in Progress

Analysis of sugars in early and late sap samples collected in the spring of 1989 and 1990 in Milton (Site #45, multiple collection) and Peterborough (Site #73); pH of sap; and micro and macro nutrients are in progress. Statistical analysis will be undertaken after all the experimental data has been collected.

PRELIMINARY CONCLUSIONS

1. Total sugar content and pH decrease as season progresses.
2. Total sugar content and pH are lower in declined trees.
3. As sucrose decreased with decline, proportion of minor sugars increases.
4. Sugar content in the early sap of declined trees is similar to the late sap of healthy trees.
5. *Al, Mn, Fe, Na,* and *Ba* levels are higher in declined trees while levels of *Ca, K,* and *B* are lower.

AP10 Modelling Concentration Fluctuations; E. Alp and A. Ciccone, Concord Scientific Corporation, Downsview, Ontario and C.S. Fung, Environment Ontario, Toronto, Ontario

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VOLUME I

SESSION B

WATER QUALITY RESEARCH

VERBAL PRESENTATIONS

82

EARLY BIOLOGICAL AND LIFE HISTORY ATTRIBUTES OF THE ZEBRA MUSSEL, *Dreissena polymorpha* (BIVALVIA: DREISSENIDAE), AND IMPACTS ON NATIVE BIVALVES IN LAKE ST. CLAIR.

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ABSTRACT

Standing crops of zebra mussels in the Great Lakes are currently increasing by an order of magnitude annually. Zebra mussels already outnumber native species of unionid bivalves by three to four orders of magnitude. They are strongly byssate and with their epifaunal mode of life are colonizing all hard substrates, a habitat that has not been previously exploited by any benthic organism. The species is exhibiting life history features which not only explain why zebra mussels are already the dominant mollusc but indicate that some native species of bivalves may even be eliminated from the Great Lakes. Compared to native species of bivalves, these features include: external fertilization which allows for greater reproduction than internal fertilization; a free-swimming larval stage for more effective and faster dispersal rates (> 250 km yr^{-1} in Lake Erie); a longer (June to October) birth period; up to four orders of magnitude greater recruitment and standing crops; and a faster growth rate. The population of *D. polymorpha* in Lake St. Clair has a different growth rate and life span than do European populations. The Lake St. Clair population is short-lived (2 years), fast-growing (about 2 cm yr^{-1}) and small in adult shell length (less than 3 cm maximum size). Massive encrustations of zebra mussels are hypothesized to have one or more of the following effects on native unionid clams: (i) impairment of normal locomotion and burrowing activities; (ii) prevention of valve closure by byssal growth of zebra mussels thus exposing the unionid to predation, parasitism and environmental extremes; (iii) prevention or limitation of valve gaping to affect normal metabolic functions for feeding, growth, respiration, excretion and/or reproduction; (iv) interference of normal functioning of the siphons and processes associated with them (e.g. respiration and feeding); (v) stripping the water of food and nutrients making little or none available to the unionid host which may ultimately starve to death; (vi) cause shell deformities that may ultimately result in premature death of the unionid; (vii) smothering by complete occlusion of the siphon region.

INTRODUCTION

The zebra mussel is a new bivalve that was introduced into the Great Lakes three years ago in the freshwater ballast of ocean-going ships from Europe (Hebert et al 1989). In the worst-case scenario, it has the potential to not only become the most serious and devastating pest of any exotic species ever introduced to North American surface waters, but also to completely alter the ecology of the Great Lakes. For more than 100 years the Europeans have witnessed its ability to (i) clog intakes and distribution pipelines in industrial and domestic facilities; (ii) corrode steel and iron pipes; (iii) taint and contaminate potable water supplies; and (iv) encrust hulls of boats and ships (Clarke 1952; Mackie et al 1989). In only three years, utilities, industries, water treatment plants and boaters on Lake Erie and Lake St. Clair have already seen these effects and, in addition, have documented: (v) fouling and rendering useless fishing gear and navigational aids (e.g. buoys); (vi) reduction, or possibly elimination, of the recreational and aesthetic value of beaches and shorelines; (vii) potential displacement of native species of bivalves; (viii) alteration or even destruction of fish habitats; and (ix) changes in the physical limnology (e.g. Secchi depth) of infested lakes (Lakes Erie and St. Clair).

The epicentre of zebra mussel invasion for the Great Lakes, and ultimately for all North American surface waters, is Lake St. Clair (Hebert et al 1989) where three generations now flourish. We anticipate that the standing crop of this newly introduced species will continue to increase during its early colonization phase, and then crash to a base level. This paper reports the current standing crop of zebra mussels in Lake St. clair and the apparent increase in their numbers since 1988 when Hebert et al (1989) described the first record. Since Lake St. Clair is the epicentre of dispersal for the zebra mussel, the lake will form an excellent model for predicting the biology, ecology and impact of the zebra mussel in other lakes. The objective of this study is to collect baseline data to determine annual changes in size, age and growth rate of the population, size, age and growth rate of individuals, sex ratio, fecundity, birth period(s), larval development and growth rate, dispersal rate and the impact on native species of Unionidae bivalves. These data will be used in models to determine the time required to attain peak population standing crop (i.e. the population "explosion" period), the maximum standing crop attained, the time to attain the minimum population standing crop (i.e. population "crash" period), the minimum standing crop attained, the mean population standing crop attained, and the short term (1 to 3 years) and the long term impact of zebra mussels on the native unionid bivalves of the Great Lakes.

METHODS

At two week intervals from May 2, 1989 to September 15, 1989, then monthly in October, November and December, 1989, 3 to 5 rocks were collected from Lake St. Clair at Puce, Ontario. The rocks varied in size from approximately 5 cm diam to 30 cm diam. Each rock was considered a sampling unit (replicate). All mussels were scraped off the rocks. At each sampling event, 10 to 20 individuals representing all length classes were randomly selected from one or all of the rocks and fixed immediately in Bouin's fluid for histological examination of gametogenesis and sex ratio; 75 to 100 individuals representing all size classes were randomly selected from one or all of the rocks for determining length-dry weight (on fresh specimens) relationships; and the remainder were preserved in 70% ethanol for deriving length-frequency histograms. The histograms were used to determine: (i) population age and size class structure; (ii) mean growth rate of each age class (cohort); (iii) life span; and (iv) birth period. The growth rate of the 1989 cohort was determined by placing a cement block in 0.6 m of water and measuring at two week intervals the increase in growth in shell length of newly settled mussels.

The mean population size at each time interval was determined by enumerating the mussels on each rock surface. The surface area of the rock was determined by placing aluminum foil around the part of the rock surface that was infested with mussels. The foil was pressed into crevices and around protuberances and any excess foil in folds resulting from this procedure was cut off. The foil was removed from the rock and the area of the foil was determined with a planimeter. The standing crop on each rock (sampling unit) was expressed as number per square metre.

The birth period was also determined by the appearance of larvae collected in student plankton samplers (mouth 20 cm diam, mesh 70 u) taken at the same sampling intervals as for adult mussels. The plankton sampler was simply swept back and forth several times in the top 0.3 m of water and the plankton collected was preserved in 5% formalin. Two of these samples were collected, followed by three, 15-L Schindler-Patalas trap samples for determining the mean abundance of veliger larvae in the water.

The sex ratio was determined from histological examination of 40 specimens fixed in Bouin's fluid. Soft tissues were removed from the shell, embedded in wax, sectioned at 6 um using a Spencer model 820 microtome and stained with Harris' modified hematoxylin and counter stained with eosin, following methods in Humason (1962). Only the posterior part of the visceral mass containing the gonad was sectioned. The period of gametogenesis and length class at which gametogenesis begins were determined from histological examination of three specimens in each of four length classes (0 to 5 mm; 5 to 10 mm; 10 to 15 mm; and greater than 15 mm) in biweekly collections of mussels beginning May 2, 1989 and ending September 22, 1989.

Only superficial effects of zebra mussels on unionid clams were examined in 1989. The relationships between unionid size and zebra mussel abundance and size was determined by removing and counting all the mussels, measuring the shell length of at least 50 mussels selected at random from each unionid shell, and then plotting the number and mean length of the zebra mussels against the shell length of the unionid. Curvilinear regressions were calculated for each plot using SAS software.

The dispersal rate of zebra mussels upstream and downstream of Lake St. Clair was determined from the appearance of larvae in zooplankton samples and newly settled adults on concrete blocks at each of twelve stations: Bright's Grove on Lake Huron; Corunna and Port Lampton on the St. Clair River; Stoney Point, Belle River and Puce in Lake St. Clair; Amherstburg in the Detroit River; Wheatley, Port Stanley, Port Dover, Long Beach in Lake Erie; and Niagara-on-the-lake in lake Ontario. Zooplankton samples were taken with a student plankton sampler with 20 cm diam mouth and a nylon mesh with 70 u mesh openings. The concrete blocks measured 10.16 cm high, 20.32 cm wide and 40.64 cm long (4 in X 8 in X 16 in) and were placed in 0.6 m of water at each each station. Zooplankton samples were taken and concrete blocks were examined at two week intervals beginning May 15 and ending November 15, 1989.

RESULTS AND DISCUSSION

The population size class structure of *Dreissena polymorpha* in the summer and fall of 1989 in Lake St. Clair is shown in Figs. 1a to 1g. Three distinct cohorts are present through most of the year, the dominant age class being one-year olds. The smallest individuals appear on two occasions, once in the late spring to early summer (late June to early July) and again in late October to early November, suggesting two annual recruitment events (birth periods), although recruitment is continuous throughout the summer. The disappearance of the oldest (largest) age class by mid summer suggests that most individuals live only three years in Lake St. Clair. This is intermediate between native sphaeriid bivalves (a few months to two years (Mackie 1980)) and unionid clams (up to twenty years Clarke 1973)). Moreover, the birth period of sphaeriid bivalves is usually confined to a few weeks in the summer (Mackie 1980) and of unionid clams to either the spring or summer (Clarke 1973).

The growth rate curves of each age class (cohort) are shown in Fig. 2, with the dates representing the time of birth. The spring 1989 cohort was born on June 27, 1989 (57 days) and grew almost 2 cm by November 15, 1989 (194 days), with a mean growth rate of 0.128 mm day^{-1}. The fall 1988 cohort also added nearly 2 cm in shell length within 194 days, but averaged only 0.100 mm day^{-1}. However, during the log phase of growth, the maximum growth rates of both the fall 1988 and the spring 1989 cohorts were similar, averaging nearly 0.5 mm day^{-1}. The cohort born in the spring of 1988 (apparently) also had similar rapid rates of growth and peaked, but the cohort died at the end of July, indicating that the cohort lived for only a year and a half. The 1987 cohort (apparently) was probably born in the summer or fall of 1987, giving that cohort a life span of only two years. Hence, the data suggest that the life span of *D. polymorpha* in Lake St. Clair is only two years maximum.

The data from this length-frequency analyses are supported by data obtained from the growth of mussels settling on concrete blocks placed in the water during the first week of June (Fig.2). Growth is most rapid in newly settled and first-year individuals and decreases with increasing age, which is typical for the species (Morton 1969b; Stanczykowska 1977).

The age and growth rate of *D. polymorpha* in Lake St. Clair are different than reported for European populations. The life span of zebra mussels in Europe varies between 3 (e.g. Stanczykowska 1977) and 5 years (e.g. Wiktor 1963; Stanczykowska 1964) in Polish lakes; 5 years in British reservoirs (Morton 1969b); 6 and 7 years in Swiss lakes (Stanczykowska 1977) and 6 and 9 years in some Russian reservoirs (Mikheev 1964; Lyakhov and Mikheev 1964). These variable life spans can be categorized into two groups. The first group is slow-growing, has a maximum shell length of 3.5 cm or less and is characterized by populations that live for 3 to 5 years. The group is typical of populations in Poland, Austria, Hungary, Switzerland and Russia (Mackie et al 1989). The second group is fast-growing, has a maximum shell length greater than 4 cm and is characterized by populations that live for more than 5 years. This group is typical of populations in Britain (Mackie et al 1989). The population of *D. polymorpha* in Lake St. Clair seems to be most similar to the first group of short-lived (2 years), fast-growing (about 2 cm yr^{-1}), small adults (less than 3 cm maximum size).

The allometry of shell growth is shown in Fig. 3. Shell width is described by the relationship, width = 0.048 + 0.408 length (r^2 = 0.98). Shell height is described by the relationship, height = 0.161 + 0.298 length + 0.072 $length^2$. The length-weight relationship is typical of most animals with a cubic relationship: total weight (mg) = 0.051 length[illegible]; tissue weight = 0.007 length[illegible] (Fig. 4). The allometry of shell growth is within the variations reported for British (Morton 1969b) and Polish (Stanczykowska 1977) populations of *D. polymorpha*. In Europe the length-weight relationship varies considerably among lakes (Lyakhov and Mikheev 1964; Walz 1978 a, b; Stanczykowska 1979) and over time (Stanczykowska et al 1975) and may be an indicator of environmental conditions (Stanczykowska 1979).

The mean standing crop of zebra mussels on rocks before the 1989 recruitment event (i.e. before settlement of youngest age class) was 10,045 m^{-2} (std. dev. = +/-5450 m^{-2}, range = 2,835 to 299,380 m^{-2}). The mean standing crop of mussels on unionid clams before the 1989 recruitment event was 7.86 cm^{-2}, or 78,600 m^{-2} (std. dev. = +/-10,575 m^{-2}, range = 400 to 460,580 m^{-2}) of posteriorly-exposed shell per unionid. There are significantly ($P < 0.05$) more zebra mussels on unionid clams than on rocks on a unit area basis. Regardless of which estimate is used, the mean standing crop of zebra mussels is two to three orders of magnitude greater than that of sphaeriid clams (range 20 to 125 m^{-2}, Griffiths (1987)) and three to four orders of magnitude greater than that of unionids (range 1 to 10 m^{-2}, this study and Griffiths 1987)).

Hebert et al (1989) reported a mean abundance of about 20 mussels on 10-cm long unionid shells in Lake St. Clair in 1988. In 1989, the mean abundance of zebra mussels on 10-cm long unionid clams was about 250, a 12.5 fold increase since 1988. Based on these data, the population of zebra mussels in lake St. Clair increased by at least by an order of magnitude (i.e. 10X) in one year. The mean length of unionids in Lake St. Clair in 1989 was about 8.5 cm and they supported an average of nearly 210 zebra mussels per shell (Fig. 13). The mean standing crop of unionid clams in Lake St. Clair is about 6.7 m^{-2}, yielding an average standing crop of "unionid supported" zebra mussels of 1,407 m^{-2}.

Based on histological examination of 40 specimens, the sex ratio of *D. polymorpha* in Lake St. Clair in 1989 was 3:2. Gametogenesis had already begun and gonads were ripe with both eggs and sperm in the first (May 2) collection of the year (Figs. 5, 9), suggesting that gametogenesis began in the winter or early spring. In European populations, oogenesis begins in the fall, followed by intensive growth of the oocytes in early spring (Antheunisse 1963). The sex ratio of most Polish populations of *D. polymorpha* is 1:1 (Stanczykowska 1977). Compared to native bivalves, most unionid species also have sex ratios of 1:1 (Clarke 1973); sphaeriids are hermaphroditic (Mackie 1986).

In the ovary the average size of a ripe egg is 50 um diam. The eggs possess a clear nucleus of 30 um diam and a nucleolus of 10 um diam. The immature eggs are attached to the epithelial wall of the follicle by a stalk. The diameter of the stalk decreases as the eggs ripen. When the egg is ripe it detaches from the wall of the follicle and lies free in the lumen of the ovarian follicle (Fig. 5). The micropyle denotes the point of attachment of the stalk to the wall of the follicle. Some eggs are released from the ovaries in late May (Fig. 6) but the peak period of reproduction is in July and August when most ovaries appear partially spent (Fig. 7). The ovaries are completely spent by the end of September (Fig. 8).

All stages of spermiogenesis are present by early May (Fig. 9). The enlarged semeniferous tubules contain primary and secondary spermatocytes, spermatids and mature spermatozoa. Ripe semeniferous tubules have an average diameter of 150 - 200 um. The sperm have elongated heads, averaging about 3 um in length. Ripe spermatozoa are located near the lumen of the seminiferous tubule with the tails directed toward the lumen (Fig. 9). Release of sperm appears to begin in late May (Fig. 10) but most are released by July and August (Fig. 11). The semeniferous tubules are completely spent by late September (Fig. 12).

Reproduction begins when specimens are about 5 mm in length and is complete before they reach 10 mm shell length. Nine of 12 specimens examined in the 5 to 10 mm length class were sexually mature. A greater proportion (12 of 13) of individuals in the 10 to 15 mm length class were ripe than in the 5 to 10 mm length class. In European populations, gametogenesis begins in adults of slightly larger sizes of 8 - 9 mm in shell length (Morton 1969b; Stanczykowska 1977).

Veliger larvae first appeared in Lake St. Clair (at Puce, Belle River and Stoney Point) and Lake Erie (at Wheatley) in June 14 samples. None were found in the May 28 samples, indicating that the veliger larvae appeared in both lakes sometime between May 28 and June 14, 1989. This birth period is similar to most populations in Europe (Stanczykowska 1977). The abundance of veliger larvae was not determined in 1989, but the absence or low numbers of < 1 mm length adults in late July to mid August of the length frequency plots (Fig. 1) suggest that there were two recruitment events, one in the spring and another in the late summer. If veliger larvae require one month to develop and settle, the larger numbers of small mussels in early July settled from the reproductive event in June and the large number of small mussels in September to November settled from the reproductive event in late July to mid August.

Dreissena polymorpha is the only freshwater bivalve in the Great Lakes that produces free-swimming veliger larvae. Sphaeriid clams are ovoviviparous, brooding their young in brood sacs on the inner gill of the parent, and producing 1 to 5 newborn (usually) (Mackie et al. 1976). Unionids brood glochidia in marsupia on the inner or outer gill, or both. Most species of unionid clams require a fish host for the parasitic glochidia to develop into the juvenile stage (Clarke 1973).

The infestation intensity increases with length (Fig. 13) and posteriorly exposed surface area (Fig. 14) of the unionid in a logarithmic relationship. Living unionid clams have an average infestation of about 210 (+/- std. dev. 56) zebra mussels per unionid (estimate based on counts made before the 1989 recruitment event) (Fig. 13). All eight species of unionids (living shells) found had zebra mussel infestations (Fig. 15). When the exposed surface of the unionid is covered, new recruits settle on top of older recruits so that the infestation intensity increases on larger unionids. Some infestations are invasive and prevent the unionid from closing its valves (Fig. 16a). Other infestations are so great that it was difficult to completely open the valves of empty shells or moribund individuals (Fig. 16b).

Some unionid shells carry more than 2500 zebra mussels with an average length of 4.5 mm. Using the length-weight regression given earlier, the biomass of zebra mussels supported by these unionid shells is 11.5 g (dry weight). The unionid itself weights 21 g (dry weight, indicating that some unionids are carrying more than half their weight. Indeed, some unionid shells support more than 15,000 zebra mussels (Hebert, pers. comm.) suggesting that, in extreme cases, some unionid shells are supporting up to three times their own weight. This observation, and others made earlier, suggest that the massive encrustations of zebra mussels will: (i) impair normal locomotion and burrowing activities; (ii) prevent valve closure by invasive growth of zebra mussels thus exposing the unionid to predation, parasitism and environmental extremes; (iii) prevent or limit valve gaping which may possibly affect normal metabolic functions for feeding, growth, respiration, excretion and/or reproduction; (iv) interfere with the normal functioning of the siphons and processes associated with them (e.g. respiration and feeding); (v) block the siphonal region and eventually smother the unionid; (vi) strip the water of food and nutrients making little or none available to the unionid host which may ultimately starve to death; and (vii) cause shell deformities that may ultimately result in premature death of the unionid. These negative effects do not support the conclusions of Lewandowski (1976) who found no "unfavourable" effects of zebra mussel infestations on Unionidae in Polish lakes.

When the concrete blocks were placed in the lakes in the spring of 1989, the zebra mussel had already been found as far east as Port Stanley in Lake Erie and as far west as Stoney Point in Lake St. Clair. By November, mussels were found on blocks as far east as Niagara-on-the-lake but had not been found on any blocks further west or north than Stoney Point in Lake St. Clair where they were already established. On this basis, downstream dispersal occurred at a rate of approximately 250 km yr^{-1}. Upstream dispersal was negligible within the area under study.

The zooplankton samples confirmed all the results obtained from the concrete blocks. Veliger larvae were found two weeks earlier than adults at Port Dover (August 8, 1989) and Long Beach (September 22) in Lake Erie and on the same week at Niagara-on-the-lake (November 22, 1989). Since samples were taken at two week intervals in the summer and monthly in the fall the veliger larvae (and adults) may have actually appeared two weeks earlier at Port Dover and Long Beach and one month earlier at Niagara-on-the-lake.

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CAPTIONS TO FIGURES

Fig. 1. Length-frequency distribution of *Dreissena polymorpha* in Lake St. Clair between May 2 and November 22, 1989.

Fig. 2. Growth rates of cohorts of *Dreissena polymorpha* based on data in Fig. 1. Dates represent time of birth for the cohort. See text for details.

Fig. 3. Allometry of shell growth in Dreissena polymorpha in Lake St. Clair.

Fig. 4. Length-weight relationships of Dreissena polymorpha in Lake St. clair.

Fig. 5. Section through ovary of Dreissena polymorpha collected May 2, 1989 from Lake St. Clair.

Fig. 6. Section through ovary of Dreissena polymorpha collected June 22, 1989 from Lake St. Clair.

Fig. 7. Section through ovary of Dreissena polymorpha collected August 14, 1989 from Lake St. Clair.

Fig. 8. Section through ovary of Dreissena polymorpha collected September 22, 1989 from Lake St. Clair.

Fig. 9. Section through testis of Dreissena polymorpha collected May 2, 1989 from Lake St. Clair.

Fig. 10. Section through testis of Dreissena polymorpha collected June 22, 1989 from Lake St. Clair.

Fig. 11. Section through testis of Dreissena polymorpha collected August 14, 1989 from Lake St. Clair.

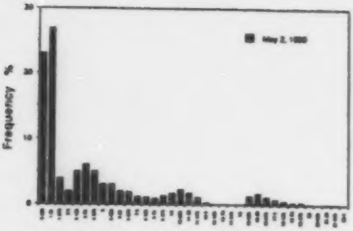
Fig. 12. Section through testis of Dreissena polymorpha collected September 22, 1989 from Lake St. Clair.

Fig. 13. Relationship between length of unionid and number of zebra mussels attached to its shell.

Fig. 14. Relationship between posteriorly exposed surface area of unionid shells and numbers of zebra mussels attached.

Fig. 15. Eight species of unionids from Lake St. Clair with zebra mussel infestations. (a) Proptera alata; (b) Leptodea fragilis; (c) Ligumia recta; (d) Lampsilis radiata; (e) Elliptio dilatata; (f) Lasmigona complanata; (g) Pleurobema coccineum.

Fig. 16. (a) Infestations by zebra mussels so intense that unioind cannot close its valves. (b) Infestations by zebra mussels so intense that unionid valves cannot be opened.


May 2, 1990
Frequency %
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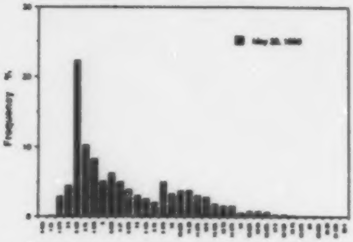
20
10
0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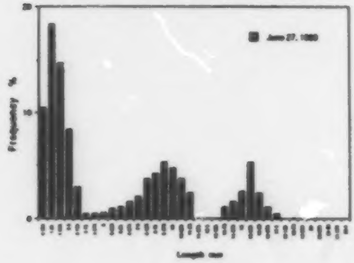
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10
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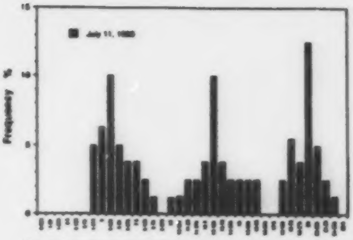
Length mm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Frequency %
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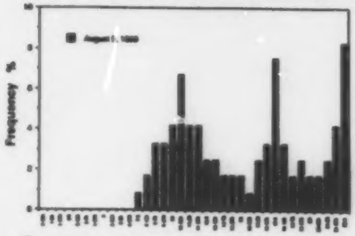
10
5
0


August 1, 1990
Frequency %
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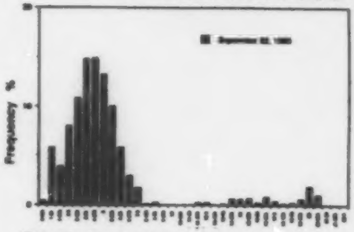
8
6
4
2
0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Frequency %
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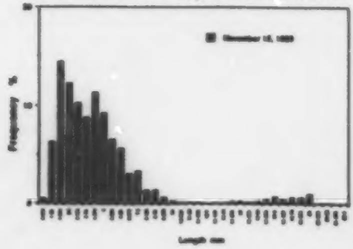
10
0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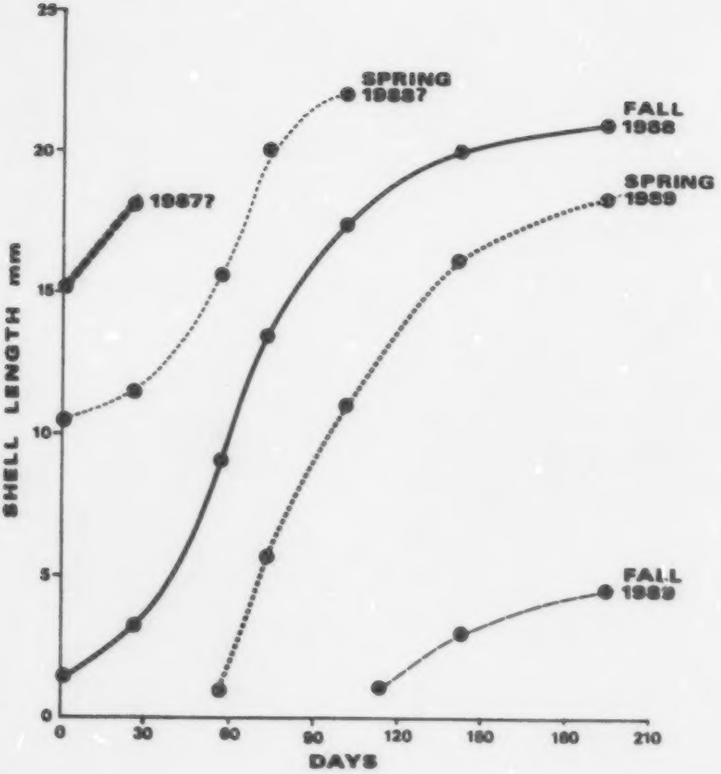
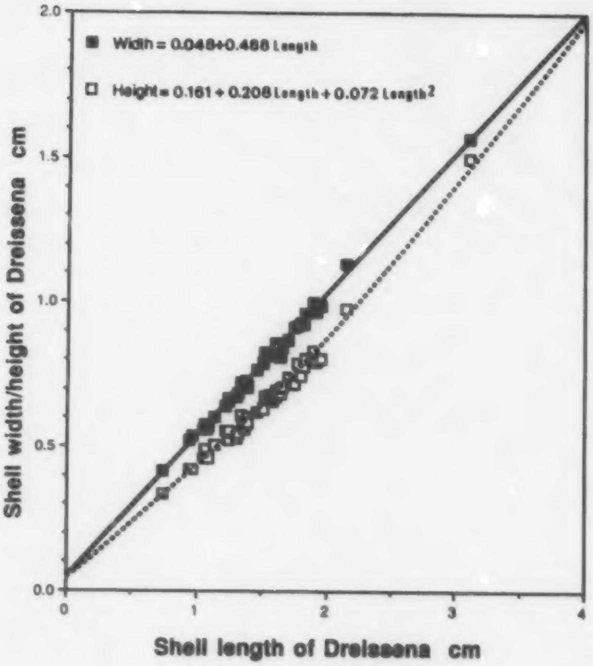
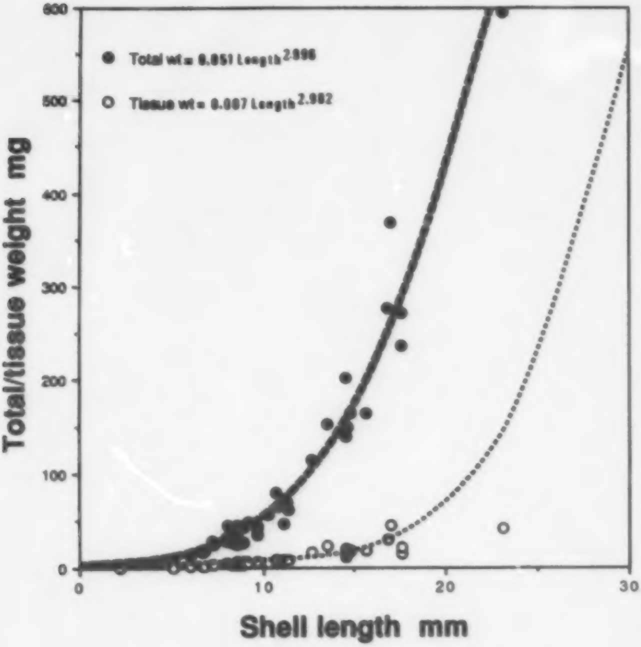
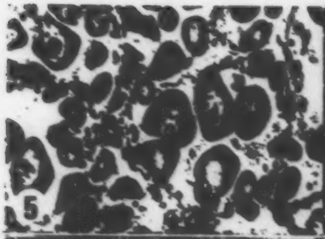
Frequency %
20
10
0
Length mm


SHELL LENGTH mm
25
20
15
10
5
0
0
30
60
90
120
150
180
210
DAYS
1987?
SPRING
1988?
FALL
1988
SPRING
1989
FALL
1989


Width = 0.048+0.468 Length
Height = 0.161 + 0.208 Length + 0.072 Length^2
Shell width/height of Dreissena cm
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
Shell length of Dreissena cm


● Total wt = 0.051 Length$^{2.996}$
○ Tissue wt = 0.007 Length$^{2.982}$
Total/tissue weight mg
600
500
400
300
200
100
0
0
10
20
30
Shell length mm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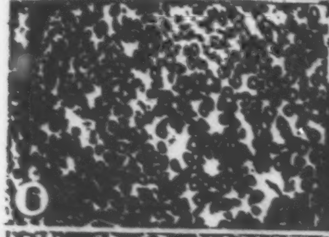
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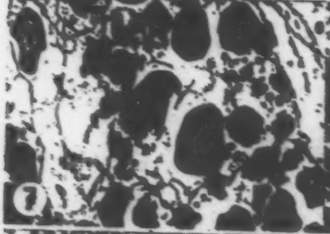
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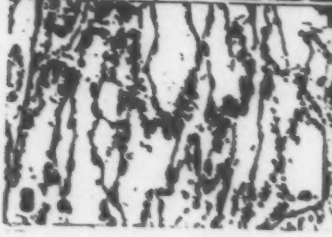
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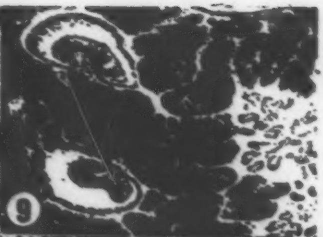
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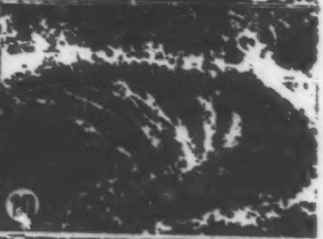
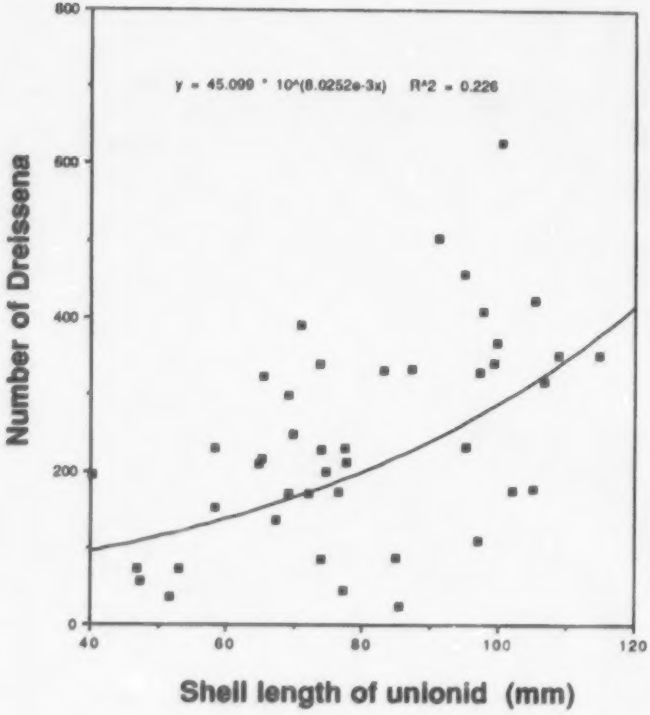
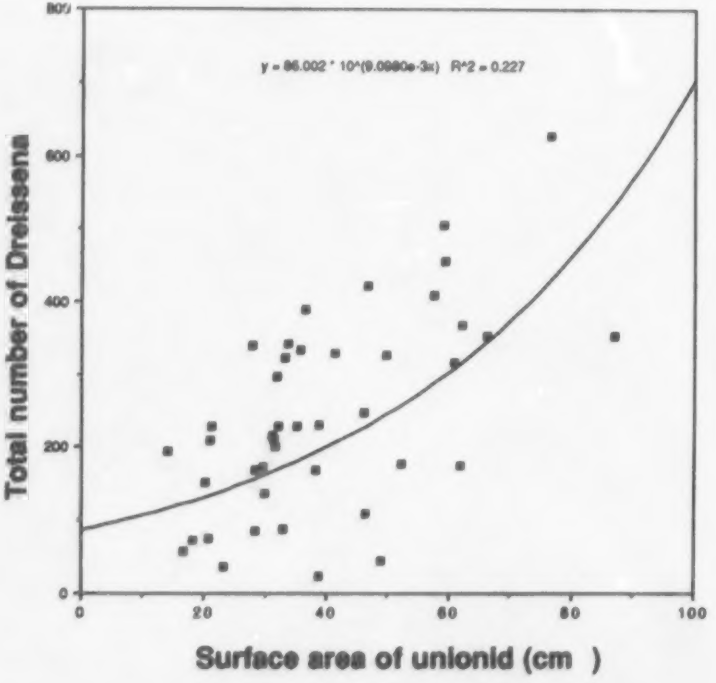
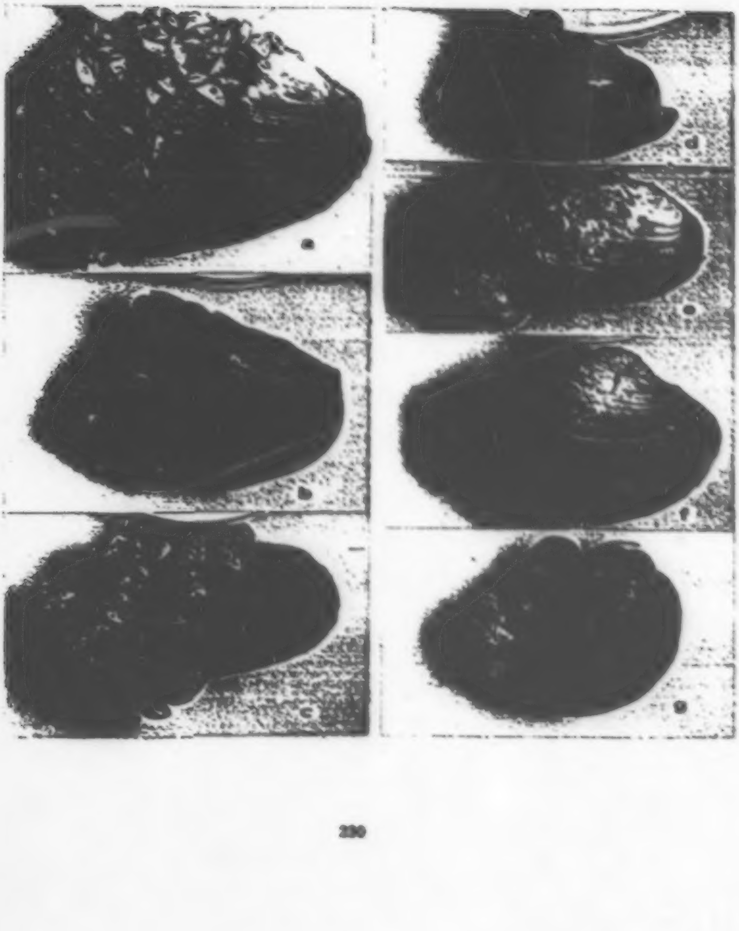

10

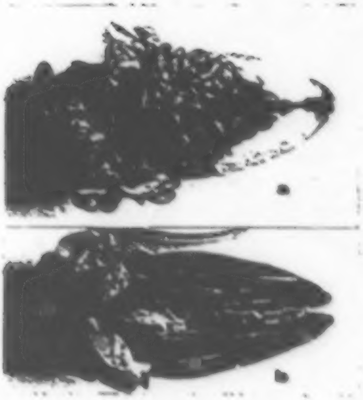
11

12


y = 45.099 * 10^(8.0252e-3x)   R^2 = 0.226
Number of Dreissena
0
200
400
600
800
40
60
80
100
120
Shell length of unionid (mm)


y = 86.002 * 10^(9.0980e-3x) R^2 = 0.227
Total number of Dreissena
0
200
400
600
800
0
20
40
60
80
100
Surface area of unionid (cm)


d



83

TOXICOKINETIC MODELLING OF MIXTURES OF ORGANIC CHEMICALS

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INTRODUCTION

Problems associated with examination of the combined effects of toxicants have been the topic of several recent reviews (U.S. EPA, 1986; de March, 1987 a,b,c; Hermens, 1989; Christensen and Chen, 1989). Current approaches to dealing with mixture toxicity are based on various methods of examining "indices" based on results largely from the mixture toxicity methodology discussed by Sprague (1970) as the "toxic unit" model. Ideally, "threshold" toxicity estimates, obtained when time and kinetic factors have been eliminated, are employed in the toxic unit equation. However, much of the aquatic bioassay data used is based on fixed duration exposures where threshold has not been confirmed or where exposures, although chronologically identical, have not been confirmed to be toxicologically similar, contrary to Sprague's advice. This approach is subject to further complications when it is used to study mixtures, as it is a static approach to what is essentially a dynamic problem. In other words, the method compares toxicity estimates obtained from bioassay data, obtained at fixed exposure durations, and ignores a very important aspect of the toxicological process, the time course of both accumulation and toxic action (Tuchy and Roth, 1988), which may be particularly problematic in mixture toxicity.

As has been noted by Sprague (1970) threshold is relatively simple to determine with single toxicants. In a mixture, the overall time-course of toxic action is affected by the kinetic factors controlling net accumulation of each component. If net uptake proceeds at different rates for each chemical, the contribution of each to the total critical residue will vary with time. Also, each will achieve its respective threshold at a different time. Thus, the toxicological effects of a mixture through time may be complicated and different than that exhibited by any of its individual components. Although time may also influence toxicodynamics as well as toxicokinetics, for the sake of simplicity it has been assumed that the biological response occurs very shortly after a critical residue has been reached in the organism.

Although useful information can be obtained with proper implementation of the basic toxic unit approach or related mixture indices, a method which incorporates exposure time and kinetics would be even more informative and begin to address the concerns of fate and toxicity modellers who must deal with time as a significant modifying factor. The one-compartment, first-order kinetics (1CFOK) model of bioaccumulation, in conjunction with the critical toxicant body residue relationships discussed elsewhere (McCarty *et al.*, 1989; McCarty 1990) should provide a more useful and informative approach. Although a similar kinetics-based development could be applied to the basic toxic unit concept, it is still "black box" in nature as little of the processes occurring in the organism are examined. The residue-based approach is easier to manipulate and both the exposure water concentrations and the residues modelled can be subjected to quantitative hypothesis testing. In this paper the simplest case, the toxicity of mixtures of chemicals with a similar mode of toxic action - similar joint action - has been considered. There are two main advantages. Firstly, for the same mode of toxic action, and similar organism characteristics, a molar concentration of a mixture should produce a similar biological response to that produced by the same molar concentration of a single chemical. For narcosis with chemicals with a log Kow greater than about 1.5 this appears to be about 2 to 6 mmol toxicant per L of fish, for small fish of about 5% lipid (McCarty, 1986, 1987, 1990; Abernethy *et al.* 1988). Secondly, the contribution of each component of the mixture to the toxic response can be followed with time. Various biological factors (size, lipid content etc.) and chemical-physical factors (hydrophobicity, pKa etc.) which influence kinetics can also be examined and be accounted for, although the latter aspect will not be addressed herein.

The objective of this paper is to model, based on 1CFOK model assumptions, the time-course and ultimate body residue at lethality for several mixtures based on data from toxicity tests with single organic chemicals. The success of the mixture modelling will be determined by comparison to bioassay results independently observed in actual mixture toxicity bioassays. The lack of measured body residues in this data set has made the task somewhat more complicated. Therefore it should be viewed as a feasibility study carried out with data not expressly obtained for this purpose. The variability may be higher than might be normally considered acceptable; on the other hand, if a trend is apparent despite the variability, it suggests that the concept is robust. In addition to data for narcotic organic chemicals, a bioassay of a mixture of 3 "polar narcotics" was available. Although complicated by the problems of ionization, and the fact that the chemicals in the mixture have dissimilar modes of action, an attempt was made to apply a similar, residue-based kinetics analysis to it.

DATA

The results of acutely toxic exposures of American flagfish, *Jordanella floridae*, (≈0.5-4 g, ≈10% lipid, ranging from 7-16%, typically 8-13%) with a variety of single chemicals and their mixtures carried out by the Aquatic Toxicity Research Group of Lakehead University (ATRG, 1987, 1988; Smith *et al.*, 1990, in press). An evaluation of the mixture toxicity of this data, based on a toxic unit analysis of 96-h LC50 data for the components of the four mixtures examined is presented below (ATRG, 1987, 1988). All seem sufficiently close to unity to conclude that these compounds are simply additive.

Triple Chlorobenzene mixture TU = 1.12 (1.01-1.24)
Double Chloroethane mixture TU = 1.11 (1.03-1.18)
Double Chloroethylene mixture TU = 1.09 (0.91-1.32)
Triple Chlorophenol mixture TU = 0.90 (0.81-1.00)

The chlorobenzene mixture experiment was problematic as the ratios between the concentrations in the 9 exposure concentrations were not constant (ATRG, 1987). The TU value for this has been recalculated herein using the three exposure levels where the ratio of the three components averaged 63%, 28%, and 9% of the respective 96-h LC50 for DCB, TCB, and TeCB. The fourth level used to estimate the TU LC50 was the next lowest exposure level with no mortality.

METHODS AND RESULTS

Deriving 1CFOK Modelling Parameters

Table 1 summarizes the parameters which have been derived for 1CFOK modelling; they have been obtained from several sources. Two critical factors, the elimination rate constant k2 and the threshold LC50 water concentration (Cw_{∞} or BCF/CL_{∞}) have been estimated by non-linear curve fitting to the raw time toxicity data (McCarty *et al.*, 1989). As noted elsewhere (McCarty, 1990), the non-linear curve fitting process is subject to statistical problems (pseudoreplication), yet more statistically valid alternative procedures are also limited by the nature of the data. Nevertheless, it is not possible to completely solve a 1CFOK model equation without at least one additional parameter (Mancini, 1983). This can be either a measured body residue for fish that have died, or a measured k1, the uptake rate constant, or a measured BCF. There are two methods of estimating a solution to this problem. The first is to estimate a BCF from established relationships between log Kow and BCF, taking into consideration the influence of lipid content on BCF. K1 and a critical body residue can then be calculated from the existing information. The second is to use an estimated critical body residue derived from another source and adjust it for lipid content. With this information k1 and BCF can be calculated from existing information.

Aspects of both approaches will be used. The first approach will be used to estimate the necessary kinetics parameters and body residues for the single chemical bioassays. BCF values, calculated from Mackay's (1982) Kow-BCF relationship using log Kow values from the MEDCHEM CLOGP 3.5 database and adjusted to 10% body-lipid content (i.e. BCF=0.10*Kow) to reflect the higher lipid content of these fish, were used to solve the 1CFOK equation. The calculated BCF values were used for consistency of approach across the three narcotic chemical groups examined. In the case of chlorobenzenes, BCFs were also measured independently in bioconcentration tests. These values were in good agreement with ones calculated from log Kow (331, 1050, 6610 versus 295, 2040, 4070, respectively). As noted in Smith *et al.* (1990), the elimination half-life for these chemicals in flagfish is similar, whether estimated from toxicity or bioconcentration bioassay data. K1 was obtained by estimating it from BCF since k1/k2 = BCF. The critical body residues presented in Table 1 were estimated as the product of calculated BCF and LC50.

The critical body residue data (mean and prediction range) obtained earlier with the fathead minnow narcotics data set - approach 2 - will be used as independent verification of the validity of the model for the three mixtures of narcotics. As well, the range of critical residue data will be used to produce model prediction limits which will be compared to the results of independently observed mixture toxicity bioassays. The adjustment for the higher lipid content of flagfish also extended to the critical body residue level. As the American flagfish were about double the lipid content of the fathead minnows, the estimated critical body residues estimated for fathead minnows (McCarty, 1990) were also doubled to 8.6 mmol/L (4.4-16.2) to approximate flagfish critical body residues. This does not indicate that the target concentration or target size has changed, just that the steady-state level fish level will be higher as there is more lipid for toxicant to partition into. As can be seen in Table 1, the estimated critical body residues for single narcotic exposures fall into this range, with the exception of 1,1,2-trichloroethane which is slightly below it.

Table 1: Information Used for Modelling the Exposure of American Flagfish to Some Organic Chemicals

Chemical	Threshold LC50 mmol/L	k2 h-1	BCF*	k1* h-1	Estimated Fish Residue* mmol/L
1,4,-dichlorobenzene	0.0144	0.0611	330	18.0	4.8
1,2,4,-trichlorobenzene	0.00549	0.0193	1050	20.2	5.8
1,2,4,5-tetrachlorobenzene	0.00175	0.0979	6610	647	11.6
1,1,2-trichloroethane	0.368	0.0676	11.2	0.763	4.1
1,1,2,2,-tetrachloroethane	0.115	0.123	107	13.2	12.3
trichloroethylene	0.222	0.398	26.3	10.5	5.9
tetrachloroethylene	0.0524	0.0454	251	11.4	13.2
2,4,6-trichlorophenol	0.0112	0.106	87	17.5	0.98
2,3,5,6-tetrachlorophenol	0.00519	0.0774	141	10.1	0.73
Pentachlorophenol	0.000766	0.0396	216	8.55	0.17

* Values calculated from as outlined in text.

The chlorophenols represent a different problem due to ionization. There are methods to correct for this (McCarty, 1990), unfortunately there is not sufficient observed residue data to confirm the best method. In this case the American flagfish data set included measured bioconcentration data and, when used in conjunction with the matched toxicity data represents the best data currently available. This toxicity and bioconcentration data were used to estimate k1 and the critical body residue. The estimated critical body residues for the chlorophenols generally fall outside the range estimated for narcotics, with pentachlorophenol, a specific toxicant (metabolic uncoupler), exhibiting the lowest residue.

Modelling Mixtures

The next task is the modelling mixtures. The essence of the approach is to model the contribution of each component independently through time and sum the results to obtain the mixture effect. This is done with the 1CFOK equation presented earlier. An example of the application to a binary mixture of chemicals A and B is presented below. The equations can be expanded to examine mixtures of more than two components. Where Cf is the body residue in the fish, Cw is the toxicant concentration in the water, BCF is the bioconcentration factor, k2 is the elimination rate constant, and t is time, the contribution of each chemical to the residue is:

$$Cf_A + Cf_A = BCF_A * Cw_A * (1 - e^{-k2_A * t}) + BCF_B * Cw_B * (1 - e^{-k2_B * t})$$

Dividing both sides of the equation by ($Cw_A + Cw_B$) and defining $f_A = Cw_A / (Cw_A + Cw_B)$ and $f_B = Cw_B / (Cw_A + Cw_B)$ produces:

$$\frac{Cf_A + Cf_B}{Cw_A + Cw_B} = BCF_A * f_A * (1 - e^{-k2_A * t}) + BCF_B * f_B * (1 - e^{-k2_B * t})$$

This assumes residue additivity and that the threshold mixture LC50 is equal to the sum of the exposure water concentrations. If the mixture critical body residue ($Cf_{AB} + Cf_{BB}$) is defined as Cf_{MB} and the mixture LC50 ($Cw_A + Cw_B$) is defined as $LC50_M$, then the equation to estimate mixture residues from LC50s and mixture LC50s from mixture residues is, respectively:

$$\frac{1}{Cf_{MB}} = \frac{BCF_A}{LC50_M} * f_A * (1 - e^{-k2_A * t}) + \frac{BCF_B}{LC50_M} * f_B * (1 - e^{-k2_B * t})$$

$$\frac{1}{LC50_M} = \frac{BCF_A}{Cf_{MB}} * f_A * (1 - e^{-k2_A * t}) + \frac{BCF_B}{Cf_{MB}} * f_B * (1 - e^{-k2_B * t})$$

The results of the first modelling exercise are presented in Table 2. In this case the objective was to take the water concentrations used in the mixture exposures and model a critical body residue estimate for each mixture. The actual exposure water levels for each chemical in each mixture were calculated from the respective single exposure threshold LC50 and the proportion of the LC50 that was used in the mixture. The fraction of the total mixture water concentration that each comprises (f_A etc.) is presented in Table 2, in brackets, as a proportion of the total molar exposure water concentration.

As can be seen in Table 2 the modelled mixture residues for the narcotics are in good agreement with what was expected. All estimated mixture residues are within the estimated adjusted critical body residue range of 4.4 to 16.2 mmol/L or kg of fish. Although the likelihood of more than one mode of action and the uncertainty caused by ionization make the estimation more speculative for the chlorophenols, the estimated residue does occur, as expected, below the range for simple narcotics.

Table 2: Modelling the Exposure of American Flagfish to Some Organic Chemicals Mixtures Based on Data Obtained with Single Chemical Exposures

Chemical	Threshold LC50 mmol/L	Proportion of 96-h LC50 in Mixture	Mixture Exposure mmol/L (Proportion)[1]		Modelled Residue mmol/L	Estimated Total Residue mmol/L
1,4,-dichlorobenzene	0.0144	0.63	0.00907	(0.865)	2.67	5.09
1,2,4,-trichlorobenzene	0.00549	0.28	0.00154	(0.12)	1.38	
1,2,4,5-tetrachlorobenzene	0.00175	0.09	0.0000158	(0.015)	1.04	
1,1,2-trichloroethane	0.368	0.79	0.291	(0.92)	3.26	5.85
1,1,2,2,-tetrachloroethane	0.115	0.21	0.0242	(0.08)	2.59	
trichloroethylene	0.222	0.70	0.155	(0.91)	4.10	8.05
tetrachloroethylene	0.0524	0.30	0.0157	(0.09)	3.95	
2,4,6-trichlorophenol	0.0112	0.68	0.00762	(0.837)	1.26	1.46
2,3,5,6-tetrachlorophenol	0.00519	0.28	0.00145	(0.16)	0.19	
Pentachlorophenol	0.000766	0.03	0.0000306	(0.003)	0.0065	

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1. The exposure concentration in mmol/L represents the actual exposure concentration of each isomer in the mixture while the proportion represents the same information in a toxic unit scale.

The results of the second modelling exercise are presented in Figures 1 to 4. In these figures the mean and 95% confidence intervals of the mean of an actual mixture bioassay are presented for various exposure times. The mean and expected range (8.6, 4.4-16.2 mmol/L or kg of fish) of the critical body residue for narcotics (Cf_B), along with the respective component proportional exposure fractions and rate constants, were used in a 1CFOK model to determine exposure water concentration necessary to generate the body residues contributed by each chemical and, ultimately, to estimate a mixture LC50 that would have generated these total mixture residues.

Chlorobenzenes

$$\frac{1}{LC50_W}=\frac{330}{Cf_B}\cdot 0.865\cdot(1-e^{-0.0611\cdot t})+\frac{1050}{Cf_B}\cdot 0.12\cdot(1-e^{-0.0193\cdot t})+\frac{6610}{Cf_B}\cdot 0.015\cdot(1-e^{-0.0079\cdot t})$$

Chloroethanes

$$\frac{1}{LC50_W}=\frac{11.2}{Cf_B}\cdot 0.92\cdot(1-e^{-0.0678\cdot t})+\frac{107}{Cf_B}\cdot 0.08\cdot(1-e^{-0.123\cdot t})$$

Chloroethylenes

$$\frac{1}{LC50_W}=\frac{26.3}{Cf_B}\cdot 0.91\cdot(1-e^{-0.308\cdot t})+\frac{251}{Cf_B}\cdot 0.09\cdot(1-e^{-0.0484\cdot t})$$

In all three cases the independently observed mixture toxicity data fell within the range predicted by the model. In each case the time course of the mean estimate was somewhat below the time course of the observed data, but the shape of the toxicity curve was similar to that of the observed data. Trial and error fitting of residues produced the optimal fit indicated in Figures 1 to 3. The critical residues employed in the optimal fit were 5.0, 5.9, and 5.8 mmol/L, respectively. This suggests that the mean critical residue for these chemicals may have actually been slightly lower that the fathead minnow estimates adjusted for differences in lipid content. As initial modelling study these results can be considered good.

The chlorophenols were a problem, both due to ionization and likelihood of different modes of action. In the interests of examining mixture toxicity with these chemicals a modified approach was used. Instead of using the adjusted narcotic critical body residues from the fathead minnow data, the critical body residues estimated for each chemical and this species in the first stage modelling were used; that is, 0.98, 0.73, 0.17 mmol/l, respectively (See Table 1). To obtain some indication of the sensitivity of the analysis to variations in body residue, a range was estimated by arbitrarily assigning a low residue value of ½ and a high residue value of twice, the each of the original estimates. The model equation is:

Chlorophenols

$$\frac{1}{LC50_W}=\frac{87}{0.98}\cdot 0.037\cdot(1-e^{-0.108\cdot t})+\frac{141}{0.73}\cdot 0.16\cdot(1-e^{-0.07\text{[illegible]}\cdot t})+\frac{216}{0.17}\cdot 0.003\cdot(1-e^{-0.0398\cdot t})$$

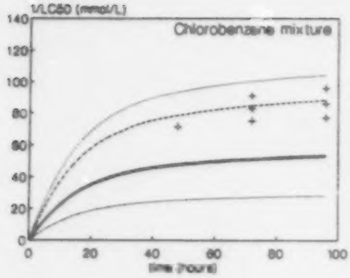

Figure 1: Mean and Range of ICFOK Mixture Model Compared with Observed Data For American Flagfish Exposed to a Chlorobenzene Mixture

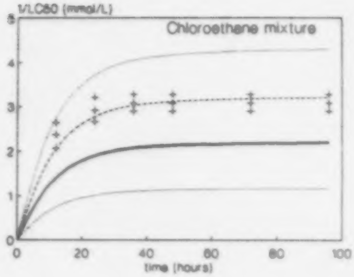

Figure 2: Mean and Range of a ICFOK Mixture Model Compared With Observed Data for American Flagfish Exposed to a Chloroethane Mixture

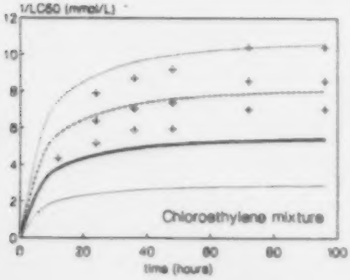

Figure 3: Mean and Range of a ICFOK Mixture Model Compared to Observed Data for American Flagfish Exposed to a Chloroethylene Mixture

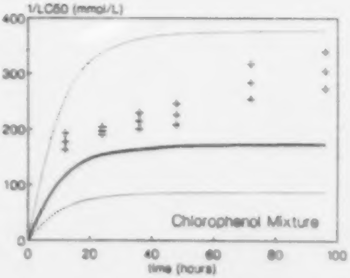

Figure 4: Mean and Range of a ICFOK Mixture Model Compared to Observed Data For American Flagfish Exposed to a Chlorophenol Mixture

Crosses represent observed LC50 data and 95% CI. Lines represent modelled LC50 estimates based on critical body residue estimates of 8.6 mmol/L of fish (solid line), 4.4 and 16.2 mmol/L (dotted lines), and optimal fit (dashed line).

As can be seen in Figure 4, the modelled data range for the chlorophenols includes the observed mixture toxicity data. The process has generated a description of the time course of an independently measured mixture toxicity bioassay, based on a mixture model employing single exposure data for each of the components, which is in reasonable agreement with the observed data.

Discussion

As noted at the beginning, success in this modelling exercise was to be determined on the basis of whether modelled molar LC50s for mixtures were in reasonable agreement independently obtained toxicity data. In the first exercise, presented in Table 2, the estimated critical body residues generated by the mixture model approach all fell in the expected range, 4.4-16.2 mmol/kg. Although less confidence is placed in the modelling with chlorophenols, due to the variability introduced by ionization and the probable presence of more than one mode of toxic action, the estimated critical body residue was below the lower limit of the expected narcotic range, as expected.

In the results of the modelling exercise presented in Figures 1 to 4, it appears that data obtained from single chemical toxicity testing results (k2 and threshold LC50), as well as data estimated independently from those toxicity bioassays (BCF and critical molar residue), can be successfully combined with the 1CFOK modelling procedure to reasonably reproduce the time-LC50 data observed in bioassays with certain mixtures of organic chemicals.

Both the threshold LC50 achieved and prediction of the intermediate LC50 observations provide confirmation of the success of the modelling exercise. The former is obvious but the latter is less so. The modelling process has synthesized 1CFOK kinetics for the mixture. In a 1CFOK model the elimination rate constant, k2, determines the shape of the curve as it approaches steady-state, while the uptake rate constant, k1, determines the magnitude of the bioconcentration above (or below) the exposure water concentration. Since BCF = k1/k2, it is possible to have a BCF which produces model data which agree with observations at threshold but does not agree with the time course of achieving threshold. Thus, if the modelled time-course is similar to the observed data it represents additional evidence supporting the validity of the model in interpreting the observations. Of course, agreement of both the modelled threshold and the time course do not guarantee validity for the model; this would require independent confirmation by means of measured kinetics and body residues. Nevertheless, the models of each of the three mixtures of narcotics appear to provide reasonable agreement with both the time course and the ultimate thresholds in the observed bioassays. The chlorophenol model can be considered reasonably successful despite the problems associated with determination of the critical body residues. The fit of the model to the data is aided by the fact that, in all cases, one chemical in the mixture dominates (63-79%). Thus, much of the model prediction of the mixture toxicity may be based on the ability to model the dominant chemical, although Hermens *et al.* (1984a&b) found that mixture toxicity of narcotic chemicals appeared to be simply additive over a wide range of mixture ratios.

It should be noted that the toxic unit approach can be used to describe the time course of mixture toxicity without knowing the critical body residue. In fact, the modelling procedures reported above are essentially identical as both employ 1CFOK assumptions and manipulate the same equations. However, the difference is that the modelling carried out above focuses on the importance of critical body residue. Thus, it can be used to both describe and interpret bioassay data, while a kinetics-based toxic unit approach without residue information is restricted, with some limitations, to describing the data. As noted in earlier chapters, the difficulties of attempting to interpret and employ toxicity bioassay data without knowledge of the critical body residue has been described by Mancini (1983) and others. Hence, the determination of threshold in a mixture is equally as important for the toxicological interpretation of the data as it is in the case of single chemical toxicity bioassays, and all of the caveats discussed earlier apply, as again the exposure water concentration(s) are being used as a surrogate for the critical body residue(s). Thus, modelling carried out above can be viewed as a logical extension of the basic toxic unit approach, which is more useful in its examination of mixture toxicity over a time-concentration continuum and more informative due to its focus on toxicant potency based on critical body residues.

This feasibility study suggests that the combination of the critical body residue concept and a simple 1CFOK model of toxicant accumulation can be used to model mixtures of chemicals with a similar mode of toxic action. Residue-based 1CFOK modelling of mixtures provides the same advantages as found in single chemical exposures. Although both the steady-state and the time course of reaching that steady-state can be described by models without the knowledge of the critical body residue (i.e. the toxic unit method can be used to describe the time course of mixture toxicity), it is not possible to determine the toxicological significance - potency of the toxicant in the organism - without that knowledge.

Conclusions

1. A one-compartment, first-order kinetics model of accumulation combined with the critical body residue concept, as defined for neutral, narcotic organics, adequately explains the observed time-LC50 data for independently observed bioassays of mixtures of chlorobenzenes, chloroethanes and chloroethylenes.

2. A similar modelling exercise for a mixture of chlorinated phenols, although more restricted due to the nature of the available data, also adequately explained the observed time-LC50 results for a chlorophenol mixture.

3. The advantages of a residue-based, toxicokinetic model approach to mixture toxicity over the "toxic unit" method include: the methodology is similar to that used for single chemical toxicity, the toxicant kinetics are a fundamental component, and the association of biological responses with molar toxicant residues in the organism focuses attention on the more toxicologically relevant site(s) of toxic action in the organism, rather than the exposure concentrations.

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B4

VERIFICATION OF A BIOCONCENTRATION-BASED MODEL FOR PREDICTING PULSE-EXPOSURE TOXICITY OF ORGANIC CONTAMINANTS TO FISH.

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INTRODUCTION

In standard laboratory toxicity tests organisms are continuously exposed to constant toxicant concentrations. In these tests, organisms generally come to a steady-state toxicant body concentration, allowing the aqueous exposure concentration to be used as a surrogate for the internal dose in forming a dose-response relationship. Water quality objectives are developed from no-effect exposure concentrations derived from such tests, and are then applied in field situations where exposures are rarely constant due to such factors as: varying rates of input, dilution, and degradation. The U.S. EPA (1979) attempted to deal with pulse and fluctuating exposures by proposing a two-number criteria (TNC), specifying a 24-h average and a peak concentration not to be exceeded. The two concentrations were based on the no-effect level and the LC50. Several studies (Ingersoll and Winner, 1982; Seim *et al.*, 1984) have shown that the proposed TNC formula did not consistently protect life. This was likely due to exposure being an inadequate dose surrogate for exposures where steady-state is not achieved.

Several studies (Hodson *et al.*, 1983; Mancini, 1983; Wang and Hanson, 1985) have used simple toxicokinetic models to estimate the dose accumulated in time-varying exposures, thus allowing for a direct examination of the dose-response relationship. We have developed a bioconcentration-based model (PULSETOX) to track the dose an organism receives under cyclic or randomly fluctuating exposure conditions. The model is an adaptation of the simple, one-compartment, first-order toxicokinetic model (1CFOK) described by Spacie and Hamelink (1982) where:

$$C_f = C_w \frac{k_1}{k_2} \left(1 - e^{-k_2 \cdot t}\right) \qquad (1)$$

C_f = toxicant concentration in fish at time t.
C_w = toxicant concentration in water.
k_1 = uptake rate constant.
k_2 = clearance rate constant.
k_1/k_2 = bioconcentration factor (BCF).
t = time.

Numerical integration techniques are used to generate a time-course output of the exposure regime and accumulated dose (Figure 1), as well as a summary of the exposure including: the maximum values of Cw and Cf achieved, and the area under the curve for exposure and dose. Since the model has input variables describing the chemical (Kow, BCF, k_2), the organism (weight, lipid content), and the exposure (concentration, duration, frequency), it forms a framework for hypothesis testing.

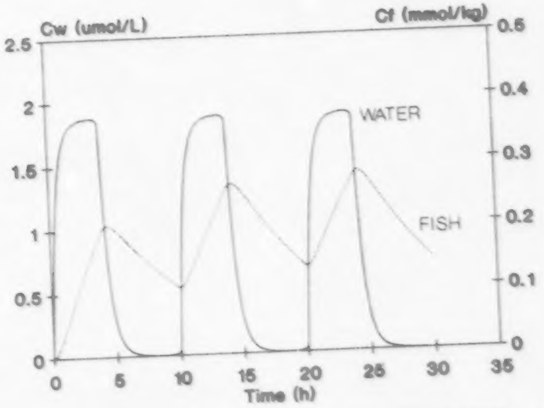

Figure 1. Example of graphical output of time-course for Cw and Cf from PULSETOX model.

Since the organism is considered as a single compartment in the model, prediction of effects are based on the whole body toxicant concentration. For lethality, predictions of effects are based on the maximum dose accumulated, with a lethal effect resulting from the organism reaching a certain critical dose (Cfr) which is characteristic of the toxicants mode of action. For narcotic organic chemicals, which include the majority of industrial organic compounds (Veith *et al.*, 1983), the median lethal Cfr value is in the range of 3 to 6 mmol/kg. For pentachlorophenol (PCP), which acts as a metabolic uncoupler, the lethal Cfr measured in fathead minnow was 0.28 mmol/kg (Spehar *et al.*, 1985). Since the value of Cfr for a chemical can be estimated as the product of the threshold LC50 and the BCF, the Cfr may also be considered as an estimate of the LD50 (McCarty, 1990). The model may also be used in a backward fashion, and work from the Cfr to predict the pulse LC50 for any defined exposure regime.

This paper reports on the initial testing of the PULSETOX model with a set of 26 pulse-exposure lethality tests of PCP to larval fathead minnow (*Pimephales promelas*). The working hypothesis for the model is that the pulse LC50 (median lethal exposure regime) defines the exposure required for an organism to accumulate a dose equivalent to the lethal Cfr or LD50. Also included in the study is direct verification of the lethal Cfr value for PCP.

MATERIALS AND METHODS

A set of continuous and pulse-exposure lethality tests for PCP were conducted with larval fathead minnow (48 to 72-h post hatch) in a flowthrough exposure system. Toxicant delivery to the exposure system was controlled with an automated multi-channel peristaltic pump. A continuous exposure test was run to define the threshold LC50 and toxicity curve. A total of 26 pulse-exposure lethality tests were conducted including seven single-pulse tests ranging from 2-h to 48-h, and 19 multiple pulse tests. Multiple exposures were simple repeating cycles, with each cycle consisting of a pulse and an interval prior to the next cycle. For example, Figure 1 shows the form of the exposure for three pulses, four-hours long with a six-hour interval. Each test consisted of five exposure levels plus a control, with 10 to 20 larvae used per level. All tests were run for 144-h to allow for observation of post-exposure mortalities.

Exposure chambers were 6 l glass aquaria which received 0.2 L water/min, giving a 95% molecular replacement time of 2 h. The resulting form of individual pulses were similar to those shown in Figure 1. Exposure conditions for all tests were: temperature, 25±0.5°C; pH, 7.9 to 8.1; total hardness, 275±5 mg/L as $CaCO_3$; alkalinity, 237±3 mg/L as $CaCO_3$; dissolved oxygen, 7.5±0.2 mg/L. Aqueous toxicant concentrations were measured daily during the continuous-exposure test, and at the end of each pulse to define the peak exposure concentrations achieved. Observations for mortalities in the continuous-exposure test were made at 1, 2, 4, 8, 16, and 24-h, and at least daily thereafter. Observations during the pulse tests followed a similar pattern but included at least one observation per pulse cycle.

Median lethal concentration (LC50) were calculated by the trimmed Spearman-Karber method (Hamilton *et al.*, 1977) using measured toxicant concentrations. For the pulse-exposure tests, LC50 calculations were based on the mean peak aqueous concentrations for each exposure regime. Expressing the pulse-LC50s in terms of peak exposure concentration allows the median lethal exposure regime to be reconstructed easily in modelling. The PULSETOX model was then used to estimate the maximum PCP residue accumulated by fish in the median lethal exposure regimes. The toxicokinetic parameters employed in modelling were determined in two ways: from [^{14}C]PCP accumulation studies; and by fitting the 1CFOK model to the toxicity curve derived from the continuous exposure test following the method described by McCarty *et al.* (1989). The [^{14}C]PCP accumulation study yielded the following kinetics estimates: BCF, 286; k_1, 76.17 h^{-1}; k_2, 0.266 h^{-1}. The toxicity-derived kinetics estimation method yields an estimate of the threshold LC50 and the k_2 which was 0.212 h^{-1}. This value is similar to the ^{14}C-derived estimate.

Residue analysis was conducted to verify the value of the lethal dose (Cfr) for PCP. This was done with larger fathead minnows (0.2 to 1.6) which were drawn from continuous exposure lethality tests which were conducted under similar conditions to those reported here. Analysis included fish that died during the tests, as well as fish from the highest exposure concentrations with survivors. This was done to determine whether whole body toxicant residues could delineate between live and dead fish and fit a classic dose-response model. Whole fish were digested in concentrated HCl, followed by extraction of PCP with hexane. The hexane extract was eluted through an Na_2SO_4 column, concentrated by rotary-evaporation, and then eluted through a silica-sulfuric acid (40% by weight) column to remove lipid. The PCP was then extracted into 5.0 mL of 0.1 M NaOH which was passed through a 0.45 µm filter prior to analysis. PCP was measured using HPLC with UV detector (235 nm) and a C-8 reverse phase column. The mobile phase was a 75:25 methanol:water mixture with 1% v/v acetic acid. The average recovery of PCP was 92.5% (±3.7%).

RESULTS AND DISCUSSION

The mean whole body PCP residue in dead fish was 0.30 mmol/kg (SD±0.02, C.V.=6.6%, n=11) and was equivalent to that reported by Spehar *et al.* (1985) (Figure 2). This measure of Cfr is a stable estimate of PCP toxicity to fish since it was independent of time to death, exposure concentration, and fish weight (multiple regression p = 0.35). The PCP residues in fish surviving 144-h at an exposure concentration equivalent to 76% of the LC50 often exceeded those measured in dead fish, with levels tending to be higher in larger fish. This appears to contradict the classic dose-response relationship, and demonstrates that the whole body toxicant residue is not an ideal surrogate for the dose at the site(s) of action. Storage or partitioning of much of the accumulated PCP away from sites of activity is the most likely explanation for this. A better understanding of this phenomenon is required if whole body toxicant residues are to be related to effects.

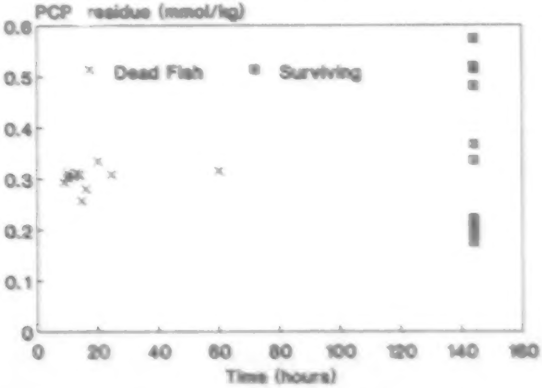

Figure 2. Measured whole body PCP residues in dead fish, and in fish surviving exposure equivalent to 76% of the LC50 for 144-h.

The continuous exposure threshold LC50 (95% C.L.) for larval fathead minnow was 0.89 μmol PCP/L (0.82-0.90). Since the lethal threshold was reached by 24-h, pulse-exposure durations less than this were emphasized in the data set. The set of pulse LC50 values are reported in Table 1. The single pulse-LC50s decreased with increasing exposure duration and form a curve similar to an ideal toxicity curve. For multiple pulses, the exposure and interval duration, as well as the number of pulses affected pulse LC50 values.

The calculated area under the exposure curve associated with each LC50 are also given in Table 1. They are similar to the average exposure concentration, and are useful since they summarize complex exposures into a single value. The pulse LC50 values do not relate well with the exposure area (Figure 3), or with other methods of expressing exposure. This demonstrates that exposure, expressed by any means, is an inadequate surrogate for dose when a steady-state is not reached.

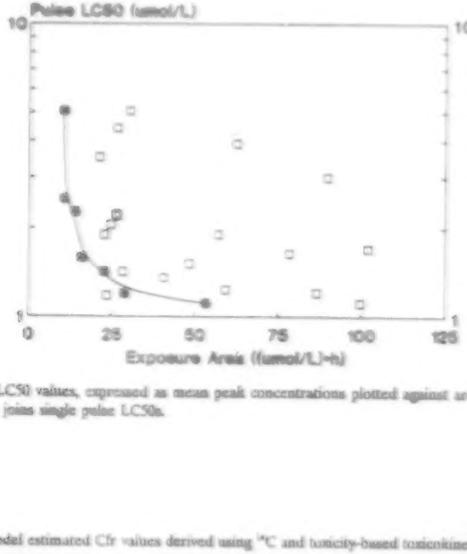

Figure 3. Pulse LC50 values, expressed as mean peak concentrations plotted against area under exposure curve. The curve joins single pulse LC50s.

The PULSETOX model estimated Cfr values derived using ^{14}C and toxicity-based toxicokinetic parameters are given in Table 1, and shown in Figures 4 and 5 respectively. Using the ^{14}C-derived kinetics, the mean estimated Cfr value was 0.38 mmol/kg fish (SD = 0.07; CV = 18.4%). For the toxicity-derived kinetics, the mean estimated Cfr value was 0.36 mmol/kg fish (SD = 0.04; CV = 18.4%). These values were nominally higher, but not significantly different than the measured Cfr value.

Table 1. Pulse LC50, based on peak water concentration, model-calculated area under curve for LC50 exposure level, and model-estimated Cfr using ^{14}C and toxicity-based kinetics estimates for PCP pulse lethality data set. Each pulse exposure test is defined on the basis of pulse duration, interval between pulses, and number of pulse exposures.

Pulse Definition			Pulse LC50 (95% C.L.) (μmol/L)	Summed LC50 Exposure Area ((μmol/L)·h)	Model Estimated Cfr (mmol/kg fish)	
duration (h)	interval (h)	number			^{14}C	Toxicity
2	-	1	5.04 (4.24-5.98)	10.02	0.52	0.45
	6	3	3.51 (3.11-3.95)	20.95	0.42	0.39
	6	15	3.00 (2.63-3.41)	89.55	0.36	0.34
	16	3	4.40 (4.13-4.70)	26.31	0.46	0.41
	16	8	3.91 (3.16-4.84)	62.33	0.41	0.36
	22	3	5.04 (4.24-5.98)	30.11	0.52	0.45
4	-	1	2.52 (2.35-2.71)	10.03	0.44	0.38
	6	3	1.89 (1.81-1.99)	22.63	0.36	0.33
	6	12	1.64 (1.45-1.85)	78.31	0.31	0.29
	16	3	2.05 (1.88-2.24)	24.52	.036	0.32
	16	8	1.51 (1.31-1.74)	48.15	0.27	0.24
6	-	1	2.27 (2.08-2.50)	13.57	0.50	0.46
	6	2	2.18 (1.86-2.57)	26.08	0.51	0.47
	6	10	1.70 (1.39-2.08)	101.69	0.39	0.37
	18	2	2.20 (1.89-2.56)	26.36	0.49	0.43
	18	5	1.91 (1.53-2.38)	56.92	0.42	0.38
10	-	1	1.58 (1.47-1.71)	15.74	0.41	0.39
	6	2	1.18 (1.08-1.29)	23.64	0.31	0.30
	6	9	1.11 (1.02-1.22)	99.66	0.30	0.29
	22	2	1.42 (1.34-1.50)	28.21	0.37	0.35
	22	3	1.35 (1.23-1.48)	40.41	0.35	0.33
16	-	1	1.42 (1.25-1.61)	22.56	0.40	0.39
24	-	1	1.20 (1.05-1.37)	28.63	0.34	0.34
	24	2	1.23 (1.06-1.45)	59.06	0.35	0.36
	24	3	1.21 (1.08-1.36)	86.47	0.36	0.36
48	-	1	1.11 (0.99-1.25)	53.16	0.32	0.32

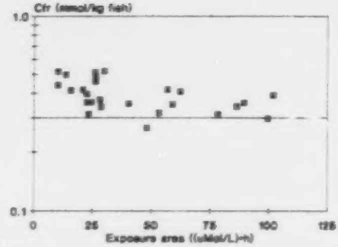

Figure 4. PULSETOX-estimated Cfr values for PCP pulse-exposure data set using ^{14}C-derived kinetics parameters. Mean measured Cfr is shown as horizontal line (Cfr = 0.30 mmol/kg).

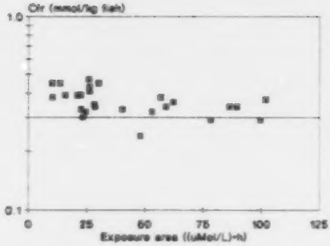

Figure 5. PULSETOX-estimated Cfr values for PCP pulse-exposure data set using toxicity-derived kinetics parameters. Mean measured Cfr is shown as horizontal line (Cfr = 0.30 mmol/kg).

Figures 4 and 5 show that the model tended to overestimate the Cfr values for the exposures with a lower exposure area, or short duration exposures. This overshoot effect could arise if there were a lag in organism response after accumulating the lethal dose. This is also reflected in linear regressions between observed and predicted pulse LC50s since the slopes exceed unity.

For ^{14}C-derived kinetics:

$$\text{pred. LC50} = 1.79\ (\text{obs. LC50}) - 0.86 \quad (p < 0.001,\ r^2 = 0.965,\ n = 26)$$

For toxicity-derived kinetics:

$$\text{pred. LC50} = 1.53\ (\text{obs. LC50}) - 0.58 \quad (p < 0.001,\ r^2 = 0.967,\ n = 26)$$

Based on the lower slope, the toxicity-derived kinetics were better in predicting pulse LC50 values. This may be due to the incorporation of both accumulation and response information into the k_2 estimated by this means, thus accounting for some part of the response lag. Further improvement on predictability may be achieved by using the k_2 estimated from a toxicity curve constructed from the set of single pulse LC50 tests. This resulted in a lower k_2 estimate of 0.122 h^{-1}. Using this value in the PULSETOX model yielded a mean estimated Cfr value of 0.30 mmol/kg fish (SD = 0.04; CV = 13.5%), equivalent to the measured value. Using the pulse-estimated kinetics, the model demonstrated an excellent capability to predict pulse LC50 as shown by the following regression:

$$\text{pred. LC50} = 0.99\ (\text{obs. LC50}) - 0.06 \quad (p < 0.001,\ r^2 = 0.940,\ n = 19)$$

The LC50 values for single pulse-exposures were exluded from this regression to avoid pseudo-replication. While predictability was dependent on the kinetics used, the model showed a robust ability to account for the variability in pulse LC50 values, as shown by the high r^2 for each regression.

Overall, the PULSETOX model provides a useful deterministic approach for predicting effects of time-varying exposures. This study clearly shows that toxicokinetics forms the critical link between exposure and dose necessary for evaluating toxicity resulting from non-steady-state exposures. The critical body residue concept employed here should also be applicable to other complex exposure problems such as mixtures and sediments.

Acknowledgement: Dr. D. Mackay, and Dr. L.S. McCarty provided valuable assistance in developing the PULSETOX model.

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B5

MAPPING LAKE WATER QUALITY CHARACTERISTICS USING LANDSAT THEMATIC MAPPER DATA

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INTRODUCTION

This report provides a summary of some of the most recent and planned activities associated with our efforts to derive relationships between lake water quality and satellite reflectance data (R.A.C. Project No. 354G). The study area of greatest emphasis has been in eastern Northern Ontario, defined approximately: from Highway 11 (Hearst to Cochrane) south to the North Channel of Georgian Bay; and from the eastern shores of Lake Superior to the vicinity of North Bay. A second area of interest has been the Quetico region of Northwestern Ontario; and a final region, not yet sampled, the area south of Lake Nipissing which we refer to as the Algonquin/Dorset area.

Over the past three years, through the annual M.O.E. Technology Transfer Conference, we have outlined various strategies for describing the relationships between and predicting selected water parameters (notably Secchi disc depth and dissolved organic carbon concentrations; discrimination between acidic and non-acidic lakes; and discrimination between lake groups of significant trophic status differences) using reflectance data recorded by a number of remote sensors. The major sensor, given that our prime task was to examine satellite data, has been the Thematic Mapper (TM) on board Landsats 4 and 5.

Those efforts are continuing, with a number of planned innovations to the overall water quality-reflectance research thrust. In addition, however, we are now faced with providing a means to illustrate those derived water quality-reflectance relationships for a very large area of the Province; and also to provide an efficient means of updating our databases with new information derived both or either from *in situ* lake water samples and satellite reflectance data. Thus, a significant portion of our attention at present has turned to the problems of computer mapping and relational database management systems (RDBMS). The computer mapping/RDBMS programme is being facilitated by the integration of remote sensing and geographical information systems (GIS) technologies.

WATER QUALITY - REFLECTANCE ASSESSMENTS

Acquisition of Spectral Reflectance Data for Northeastern Ontario Lakes

Lakes, lakes, lakes! It has been said that there are 250,000 lakes in the Province of Ontario. We believe it, and then some! For the better part of the Summer of 1990, we have been gathering Landsat TM spectral data for all lakes of "sufficient size" in the area described above as our main study region. At this point close to 85% of the study area has been surveyed.

The criteria that we are using as "sufficient size" are that a lake must contain approximately 10 Landsat picture elements or pixels (4-5 ha) and there must be more than one pixel on either side of the lake centroid. We are trying to avoid 'mixels' which are combinations of water-terrain reflectance and to avoid bottom effects as much as possible. While the final statistics have yet to be computed, most of the sampled lakes are 10 ha in size or greater. Many lakes that are 10 ha or smaller (and even some that are larger) have not been selected because they are too long and thin to meet the criteria above.

This sampling protocol should significantly add to the database of the Ontario Ministry of the Environment, especially in the proportion of smaller Ontario lakes. Given the difficulties of providing provincial estimates of lake acidification (Neary et al., 1990), we are confident that these data will be beneficial for lake water quality assessments and monitoring.

Once all the candidate lakes have been selected, TM reflectance and area statistics will be computed and then associated (using multiple regression and multivariate discriminant analyses) with the limited water quality characteristics that have been provided from MOE and MNR lake inventories. Based on the successful derivations of associations between lake water quality and Landsat TM reported in the past (Pitblado 1987; Pitblado et al. 1987; Pitblado 1988; Pitblado and Dempsey 1989), we do not anticipate difficulties here.

Acquisition of Spectral Reflectance Data for Algonquin/Dorset Area Lakes

Following the same protocol as outlined above, Landsat TM reflectance data for lakes located south of Lake Nipissing are to be acquired. For that area we have one mid-summer digital image and a late-spring image. All of the previous work that has been undertaken during this research project has focused on the use of mid-summer imagery -- at the same time as or very close to the dates when lake water quality samples have been gathered. If the late-spring image is employed, it will be our first temporal assessment of associations between lake reflectance and lake water quality.

Bowland Lake

The majority of water quality studies based on the use of remotely sensed data (our own and elsewhere) has focused spatial parameters. That is, given satellite data (and in some instances other sensors) of the same or similar date, researchers have identified between-lake or within-lake differences. Both qualitative and quantitative assessments of differences are now fairly common. Very few temporal assessments have been undertaken (Pitblado 1990). And to our knowledge, no temporal assessments using satellite data have been attempted for an acidic lake that has been subjected to an acid neutralizing programme.

Our final task in this part of the research programme will be to examine the temporal water quality-spectral characteristics of Boland Lake (47°05'N, 80°50'W). Ten dates of imagery (from 1973 to 1986) are available for this assessment. Theoretically these dates nicely span the before-during-after time period with respect to the neutralization of the lake in August of 1983. Some of these images may have to be eliminated from the analysis because (at least as viewed from poor quality microfiche) there is some cloud or haze above or nearby Bowland Lake.

This will be an extremely interesting experiment, first because of the water quality changes known to have occurred over this time period (Keller et al. 1990; Molot et al. 1990). And second, because the images are derived from four different Landsat satellites using two different sensors (the MSS, multispectral scanner of Landsats 1,2,3 and the TM, thematic mapper of Landsat 5).

Modelling

The work outlined above and described in more detail elsewhere clearly identifies that relationships exist between water quality parameters (or groups of parameters) and water colour, and that satellite sensors can measure water colour with sufficient sensitivity to monitor changes in water quality. A complementary, and necessary, next step is to develop a fundamental understanding of why these relationships exist and what controls them. Field investigations were recently initiated for this task by Ann Gallie (personal communication, Laurentian University) which will further our ability to interpret water colour and water clarity in terms of water quality and to understand the conditions under which empirical relationships will hold (see also, Pitblado and Gallie 1990). Gallie's work focuses on the development of a theoretical optical water-quality model for Northern Ontario. The model is based on the reflectance equations of Gordon et al. (1975) relating reflectance to the inherent optical properties of the water body as well as accounting for atmospheric and water surface effects (Gallie, 1990).

REMOTE SENSING - GIS INTEGRATION

As suggested above, hundreds of lakes in Northeastern Ontario are being examined through this research project. The data associated with each lake consists of: the mean spectral characteristics for each of seven Landsat TM spectral bands for ALL of the sampled lakes; the mean spectral characteristics for each of four Landsat MSS spectral bands for 90 lakes in the immediate Sudbury area; the mean spectral characteristics for each of eleven airborne Daedulus spectral bands for 20 lakes north of Lake Wanapitei; and up to 30 water quality parameters (e.g. pH, DOC, Secchi disc depth, Ca, Mg, chlorophyll a, etc.) for a relatively small fraction of those lakes sampled using the satellite imagery. The latter data were derived from field studies, undertaken by the senior author, the Ontario Ministry of the Environment, or the Ontario Ministry of Natural Resources. The handling of this spatially and temporally diffuse data has lead us to employ the techniques/technology of geographical information systems (GIS).

Geographical information systems are fundamentally collections of computer hardware and software modules designed for the capture, storage, display, analysis, and output of spatially related data. Goodchild and Brusegard (1989) have identified 65 generic GIS functions and the fact that major systems often have over 1000 commands or functions. The function that we are presently grappling with, as we integrate remotely sensed data into a commercial GIS, is image rectification and/or data transfer.

The geometry of Landsat satellite orbits is such that some form of rectification is required for compatibility with a GIS where a reference coordinate system is the foundation of the data base. This coordinate system, given that when working in Ontario and Canada with digital maps from the Ontario Basic Mapping System or the National Topographic System respectively, is the Universal Transverse Mercator (UTM) projection.

Standard procedures exist for the rectification of Landsat imagery to a UTM coordinate system, i.e. to transform image coordinates to ground coordinates. The three most popular procedures are (after Silfer 1988):

a) nearest neighbour - uses the intensity of the closest pixel to assign a value to the output pixel.

b) bilinear interpolation - uses four neighbouring pixel's values and interpolates an output value.

c) cubic convolution - uses sixteen neighbouring pixil's input values to interpolate an output value.

For the analysis of the lakes in Northeastern Ontario, all of these procedures significantly alter the numerical values of reflectance value means in each of the TM or MSS bands. These algorithms were not designed to make the sharp water/not-water distinctions that we require in this study when moving from the raster-based data structure of our imagery to the vector-based data structure of our GIS. Consequently, we have adopted a semi-automated means of transferring imagery data to the GIS environment. It requires that: numerical lake IDs be generated which are the linking-keys between the two systems; lake reflectance means generated in the image analysis environment, i.e. no geometric corrections undertaken for the Landsat data; and then those numerical values transferred to keyed lakes in the vector-GIS environment using a standard input function of the GIS software. The data identifying the lake boundaries in the GIS system are vectors abstracted from OBM or NTS digital files based on the UTM grid system and ranging in scales from 1:20,000 to 1:250,000.

It is well known that the building stage of a GIS is the most time-consuming and laborious/tedious. We are presently going through that stage is building a GIS database for lakes in Northeastern Ontario. Once completed, we are confident that it will be ideal for analyses, mapping and monitoring lake water quality (with or without the aid of a remote sensing component).

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MULTISPECTRAL REMOTE SENSING TECHNIQUES for PAST, PRESENT and FUTURE MAPPING of CHLOROPHYLL

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Extended Abstract

Multispectral remote sensing, both from satellite and aircraft, offers the potential for large scale routine water quality monitoring. Complementary to in-situ techniques, remote sensing provides highly detailed information on the spatial distribution of suspended solids and chlorophyll concentrations.

Satellite remote sensing in the past has been hampered by the lack of spectral resolution. MONITEQ Ltd. has designed and developed an airborne digital imaging system the Fluorescence Line Imager - FLI (also known as Programmable Multispectral Imager - PMI) as a prototype for satellites which will be launched in the late 1990's.

One of the objectives of this project was to make use of the FLI/PMI's high spectral resolution to simulate data from past, present and future satellites. This has been accomplished using FLI/PMI data collected over a portion of the Lake of the Woods, Ontario. Further processing of this dataset has produced a new model for detection and mapping of inland lake surface chlorophyll concentration. The results of this new model have produced an $r2=0.96$ correlation to in-situ water samples collected at the same time as the airborne FLI/PMI data capture.

Through this project the spectral location of freshwater chlorophyll fluorescence line was identified (approximately 705 nm) using the airborne FLI/PMI sensor. Making use of the high spectral resolution we believe that a four channel sensor can be developed to map chlorophyll for Ontario's lakes. A model very similar to the marine chlorophyll Fluorescence Line Hight (FLH) technique developed by Gower and Borstad (several publications) can be applied for a very economical monitoring methodology.

We will further discuss the model optimization used to compute both turbidity and chlorophyll concentrations and identify its potential use with future satellite data.

Another objective of this study was to examine the potential of processing historic satellite (LANDSAT) databases dating back as far as 1972 which can then be reviewed and correlated to changes in water quality and establish trends. The FLI/PMI data was used to simulate the LANDSAT multispectral channels and then processed for chlorophyll and turbidity. These simulated satellite data products were compared to the output from the FLI/PMI model and to the processed results from LANDSAT data (collected the day after FLI/PMI data capture) over the same site. The results of this comparison show that the greater spectral and spatial resolution of the FLI/PMI provides the best product. However, historic satellite data can show general trends in water quality, which can provide hindsight to the resource manager.

B7

REGIONAL ANALYSIS OF LOW FLOW CHARACTERISTICS FOR CENTRAL AND SOUTHEASTERN REGIONS

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ABSTRACT

Low flow statistics for ungauged watersheds are essential for analysing water quality conditions and environmental impacts, etc. This study describes the low flow characteristics of the Central and Southeastern regions defined by the Ontario Ministry of the Environment. Four techniques for estimating low flows, i.e. regression, index, area proration and mapped isolines of unit low flows were developed and compared. Several test stations which were not included in the development of the estimation techniques, were used in evaluating the usefulness and accuracy of the various techniques. The mapped isolines method was found to give the best estimates for estimating low flows of $7Q_2$ and $7Q_{20}$.

INTRODUCTION

Low flow statistics have many uses including analysis of municipal and industrial effluent discharges into streams, instream pollutant analyses, reservoir design for low flow augmentation, environmental approvals, feasibility of small hydro developments, water supply and evaluation for water taking permits, base flow/groundwater recharge and/or contamination analysis, stream fisheries assessments, etc.

The identification of low flow characteristics within a watercourse is most easily accomplished using continuous hydrometric data recorded for the stream. One source of such information describing low flow characteristics are the "Low Flow Characteristics" maps updated by Cumming Cockburn Limited for the Ministry of the Environment (1989). However, the effectiveness of utilizing single station analyses is limited since a hydrometric recording gauge may not be located in the vicinity of the study site.

The most commonly used techniques for estimating low flow characteristics for ungauged watersheds are regression equations based on physiographic and hydrometeorologic basin characteristics, index methods, area proration, and isoline maps.

This project undertook to develop and evaluate these techniques for estimation of low flow statistics for ungauged watersheds.

A REGIONAL PROBABILITY DISTRIBUTION FOR ANNUAL MINIMUM n-DAY AVERAGE DAILY STREAMFLOWS

The development of a generalized method requires selection and use of an appropriate method for analysis of suitable single station measurements of selected low flow characterisics. In addition to a literature review of statistical hydrologic fitting techniques, a previous evaluation of the Biologically Based Low Flow Analysis Technique (Cumming Cockburn, 1990) was also utilized to confirm selection of an appropriate method. On the basis of these comparisons, the Gumbel III distribution was generally applied except for stations with large negative skewness where the 3-Parameter Log Normal distribution was used. Parameter estimation for fitting of distributions proceeded in order of maximum likelihood, smallest observed drought and moments. The results of the extreme value analysis for each station were presented elsewhere (Cumming Cockburn, 1989).

REVIEW OF LOW FLOW ESTIMATION TECHNIQUES

The use of regional regression equations is the most commonly reported technique for estimation of low flow statistics. A summary of various equations developed by others is given in Table 1.

The area proration method is currently being used by many practising hydrologists and by the Ontario Ministry of the Environment for estimation of the low flows and has previously been used by Cumming Cockburn (1990).

The index method has been used by Osborn (1974) and Cumming Cockburn (1990).

Based on the review of literature, it was expected that the regression method would outperform the other techniques.

STUDY REGION

The study was undertaken for the Central and Southeastern regions as defined by the Ministry of Environment (Figure 1). A total of 95 hydrometric stations were identified in the region based upon a screening of data including regulation, outliers, the period of record and other station characteristics. Low flow characteristics for 73 (48 and 25 for the Central and Southeastern regions, respectively) of these stations were analysed to develop the estimation techniques. Twenty-one (12 and 9 for the Central and Southeastern regions, respectively) of those stations remaining were set aside for testing of results. Prediction techniques were developed for each region and for the combined data set.

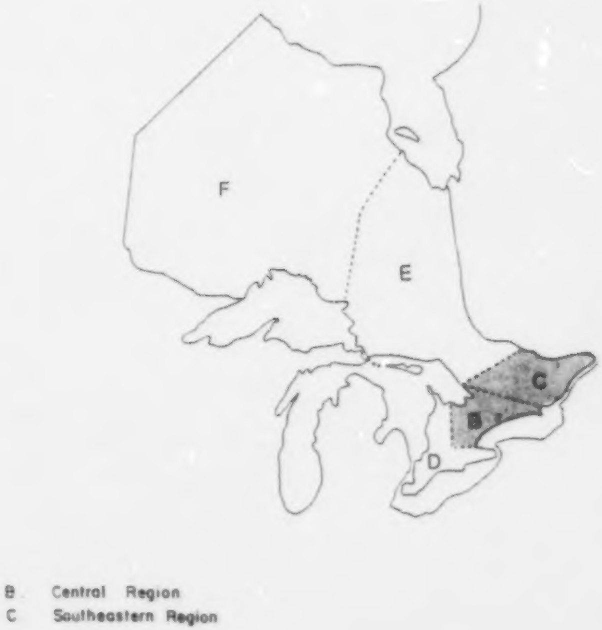
DEVELOPMENT OF ESTIMATION TECHNIQUES

Four techniques (i.e. Regression, Area Proration, Index and Isolines) for estimating low flows were developed during this study as described briefly below:

TABLE I

SUMMARY OF LITERATURE REVIEW

Study	No. of Stations	Distri-bution	Method	Parameters Examined	General Form of Equations
Boyer, 1977	12	G	Regression	DA,CO,EL,LAT,LEN WF, T_{10}, R_{10}	$\ln(7Q_{10}) = f(CO,LEN,WF,T_{10},R_{10})$
Osborn, 1974	20		Index Regression	Q7L1P,P,DA,H, CL,DD	$\log 7Q_2 = f(DA,H,Q7L1P,P)$ $\log 7Q_{20} = f(P,7Q_2)$
Condie, 1983	74	G	Regression	DA,MAP,BFI	$MED(10) = f(DA, BFI)$ $GRADMEN = f((MED(10))^{.5})$
Armbruster, 1976a	104		Regression	DA,CS,BL,EL,FC MAP,ACLS,MAS,SI	$\log 7Q_{10} = f(DA, MAP, SI)$
Armbruster, 1976b				MAP,CF,DA	$\log 7Q_{20} = f(DA, MAP, CF)$
Tasker, 1975		LN III	Regression		$7Q_{10} = f(DA, MAP, T)$
Env. Can. 1978	11	G		DA,R,AS,AL,ALS, OB,LEN,DD,SLP, EL,MAP	Correlation Matrix only produced
MacLaren Plan-search, 1981	9	Eye Fit	Regression	DA,SI,ALS	$\bar{Q}_1 = f(DA, SI, ALS)$ $\bar{Q}_5 = f(DA, SI, ALS)$
Inst. of Hydrology 1980		G	Regression	$Q_{95}(10)$,BFI,DA, MAP,LEN	$Q_{95}(10) = f((BFI)^{.5}, (DA)^{.5}, (MAP)^{.5})$ $(Q_{95}(10)) = f((BFI)^{.5}, (DA)^{.5}, (LEN)^{.5})$ $(10Q_2) = f(BFI)$ $(10Q_2) = f(BFI, MAP)$
Wright 1970			Regression	DA,BS,MAP	$MAM = f(DA, BS)$ $MAM = f(DA, BS, MAP)$
Inst. of Hydrol-ogy, 1986	232	LN	Regression	BFI, MAP, ACLS	$\sqrt{Q95(10)} = f(BFI, MAP, ACLS)$ $\sqrt{MAM(10)} = f(BFI, ACLS)$
Vogel & Kroll 1990	23	LN	Regression	DA, RELIEF	$7Q_y = f(DA, RELIEF)$
Cumming Cockburn 1990	65	3PLN	Regression	DA,BFI,LNTH	$nQ_y = f(DA, BFI, LNTH)$


F
E
C
B
D
B Central Region
C Southeastern Region

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STUDY REGION LOCATION

FIGURE - 1

1. Regression: Based upon the literature review, the following hydrometeorologic and physiographic parameters were selected for development of the regression equations: Hydrometeorologic; Mean Annual Precipitation, mm (MAP), Mean Annual Snowfall, mm (MAS), Mean Annual Runoff, mm (MAR) and Mean Annual Evaporation, mm (MAE) and Physiographic; Drainage Area, km^2 (DA), Area Controlled by Lakes and Swamps, % (ACLS), Stream Length, km (LNTH), 10/85 Channel Slope, m/m (SLP), Base Flow Index, dimensionless (BFI), Regulation Index, 1-regulated, 0-natural (RN), and Maximum Groundwater Fluctuation, m (GW).

   For development of the regression equations, $\log_{10}$, square root, squared and cubed transformations of these parameters and the following derived forms were used; Shape Factor 1 (SF1) = $DA/LNTH^2$, Shape Factor 2 (SF2) = DA/LNTH, Shape Factor 3 (SF3) = DA*SLP*LNTH/2, Infiltration/Recharge or Deep Percolation (INF) = MAP-MAR-MAS, P1 = $\{ LNTH/\sqrt{SLP} \}^{\frac{1}{4}}$ and P2 = $\{BFI/(LNTH/\sqrt{SLP}) \}^{\frac{1}{4}}$.

   The parameters MAE and GW and the derived parameters SF1, SF2, SF3 and INF were included for the first time in this study.

   Over 250 preliminary regression equations were developed in order to predict the $7Q_2$ and $7Q_{20}$ low flows as a function of hydrometeorologic and basin physiographic parameters, parameter transforms or derived transforms. The equations were developed based on different groups of parameters as summarized in Table 2. On the basis of the highest R squares and the lowest standard error of estimates and engineering judgement, the fifth set of parameters in Group II was retained along with the other groups for testing.

2. Index Method: Graphs of $7Q_2$ and $7Q_{20}$ as a function of DA were developed for the Central, Southeastern and the combined regions. The ratio of 7Qy to various nQy (n-day flows with y years recurrence interval) were determined and plotted in Figure 2 for the three regions, respectively. Also, the ratio of 7Qy to $7Q_2$ for all these regions are depicted in Figure 2. To use this method, knowing the drainage area, the $7Q_2$ flow is estimated from the relevant graph of flow versus drainage area. If another nQy flow is required, it can be estimated by using Figure 2 depending upon the region and the type of low flow to be estimated, to determine the appropriate flow ratio as a function of $7Q_2$.

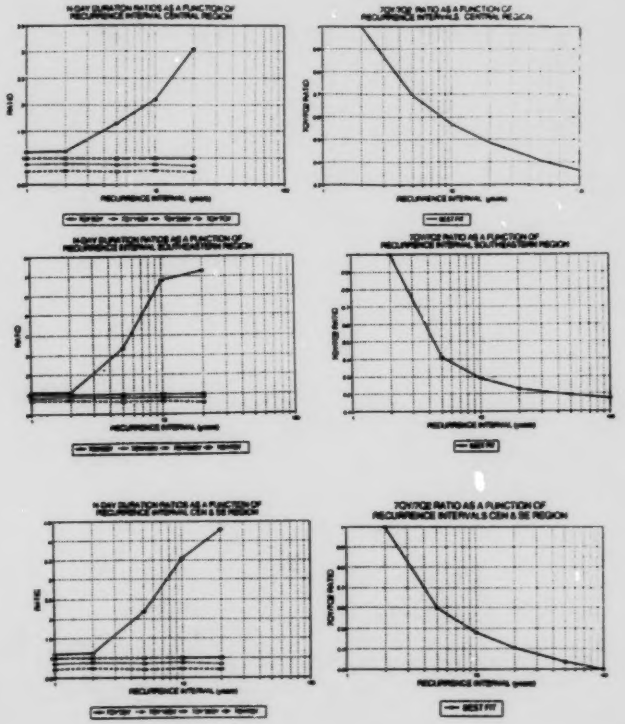
3. Area Proration: The unit area $7Q_2$ and $7Q_{20}$ low flows ($L/s/km^2$) were summarized for the stations in the region and the method of reciprocal distance was used as a weight in the proration estimate (i.e. the distance to nearby gauges would be estimated and unit values could then be weighted by the reciprocal of the distance and then averaged for the test stations).

4. Mapped Isolines Method: Isolines of unit area $7Q_2$ low flows were drawn using ditigal terrain modelling procedures and the $7Q_{20}$ low flows were estimated by using Figure 2.

Table 2: Summary of Regression Analysis

Group	Region	Parameter/Transformed or Derived Form	Low Flow	N	SEE	R^2
Group I	CN	MAP, DA, LNTH, RN, GW, BFI, MAS, MAE, SLP, ACLS and MAR	7Q2	48	0.52	0.86
			7Q20	48	0.25	0.72
	SE		7Q2	25	0.53	0.98
			7Q20	25	0.53	0.98
	CNSE		7Q2	73	0.98	0.91
			7Q20	73	0.61	0.89
Group II						
First Set	CN	GW^3, RN, MAP, Log10 MAE, SLP^3, SF2 AND Log10 BFI	7Q2	48	0.50	0.87
		Log10 GW, RN, INF, MAS, SLP^2, SF2, BFI^3 and ACLS	7Q20	48	0.23	0.76
	SE	Log10 GW, RN, INF, SF3, BFI^3 and MAS	7Q2	25	1.25	0.91
		Log10 GW, RN, INF, SF3, BFI^3 and ACLS	7Q20	25	0.81	0.90
	CNSE	GW^3, RN, MAP^3, MAR^3, MAE, MAS^3, SF3, BFI^3 and ACLS	7Q2	73	1.27	0.84
		GW^3, RN, MAP^3, Log10 MAR, MAE^3, MAS^3, SF3 AND BFI^3	7Q20	73	0.66	0.87
Second Set	CN	GW^3, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, EVA^3, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.50	0.87
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.45	0.99
			7Q20	25	0.27	0.99
	CNSE		7Q2	73	0.81	0.93
			7Q20	73	0.50	0.93
Third Set	CN	Log10 GW, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, MAE^3, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.50	0.87
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.47	0.99
			7Q20	25	0.29	0.99
	CNSE		7Q2	73	0.73	0.95
			7Q20	73	0.43	0.94
Fourth Set	CN	GW^3, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, Log10 MAE, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.47	0.89
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.47	0.99
			7Q20	25	0.29	0.99
	CNSE		7Q2	73	0.78	0.94
			7Q20	73	0.48	0.93
Fifth Set	CN	Log10 GW, RN, MAP^3, MAS^3, Log10 MAR, SLP^3, Log10 MAE, DA^3, BFI^3, LNTH^3 and ACLS	7Q2	48	0.47	0.89
			7Q20	48	0.24	0.73
	SE		7Q2	25	0.49	0.99
			7Q20	25	0.30	0.98
	CNSE		7Q2	73	0.71	0.95
			7Q20	73	0.43	0.95
Sixth Set	CN	Log10 MAS, Log10 MAR, DA^3, BFI^2 and LNTH^2	7Q2	48	0.89	0.60
			7Q20	48	0.32	0.54
	SE		7Q2	25	0.90	0.95
			7Q20	25	0.59	0.94
	CNSE		7Q2	73	1.14	0.87
			7Q20	73	0.63	0.88
Group III	CN	MAE and DA	7Q2	48	0.64	0.79
			7Q20	48	0.29	0.61
	SE	DA, MAE and BFI	7Q2	25	0.96	0.95
			7Q20	25	0.59	0.94
	CNSE	(a) DA, GW and MAE	7Q2	73	1.27	0.84
			7Q20	73	0.80	0.81
		(b) DA, BFI and MAE	7Q2	73	1.35	0.82
			7Q20	73	0.88	0.77
Group IV	CN	DA and Log [illegible]	7Q2	48	[illegible]	[illegible]
			7Q20	48	0.29	0.62
	SE	DA^3, MAE^3 and BFI^2	7Q2	25	0.81	0.96
			7Q20	25	0.52	0.96
	CNSE	(a) DA^3, Log10 MAE and Log10 GW	7Q2	73	0.92	0.92
			7Q20	73	0.51	0.92
		(b) DA^3, Log10 MAE and BFI^3	7Q2	73	0.92	0.92
			7Q20	73	0.57	0.90
Group V	CN	DA^3, BFI^3 and LNTH^3	7Q2	48	1.02	0.48
			7Q20	48	0.35	0.45
	SE		7Q2	25	1.37	0.89
			7Q20	25	0.91	0.87
	CNSE		7Q2	73	1.23	0.85
			7Q20	73	0.65	0.87
Group VI	CN	DA only	7Q2	48	1.11	0.38
			7Q20	48	0.35	0.46
	SE		7Q2	25	2.18	0.73
			7Q20	25	1.37	0.70
	CNSE		7Q2	73	1.72	0.71
			7Q20	73	0.98	0.71

N-Number of Stations SEE-Standard Error of Estimates



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CCL

RATIOS OF DIFFERENT LOW FLOWS

FIGURE - 2

TESTING OF ESTIMATION TECHNIQUES

The relative prediction accuracy of the four methods was examined using the reserved test data set and the Nash-Sutcliffe (1970) model efficiency statistic, designated as N.S.R.^{2}. As noted previously the 21 test stations were not included in the development of the regional low flow estimation techniques.) A comparison of the test statistics is given in Table 3.

1. Regression: The estimation of low flows by the regression equations using all the untransformed parameters described by Group I was poor and, therefore, not included in further discussion. The test results for the other groups are summarized in Table 3. Based on an analysis of Table 3(b), (when stations 02KC014 and 02LB013 were excluded), it was found that the form of equation based on Group IV (DA and Log_{10} MAE for the Central region and DA^3, $\log_{10}$ MAE and BFI^3 for the combined region) and Group V (DA^3, BFI^2 and $LNTH^2$) for the Southeastern region would give acceptable accuracy. It was found that the regression method can lead to satisfactory estimation of low flows in the Central region, and acceptable accuracy in the Combined Region and a satisfactory prediction of $7Q_{20}$ in the Southeastern region. The regression equations having a very high R square value for development did not necessarily give a satisfactory N.S.R.^{2} when tested using the reserved stations.

2. Area Proration: It is evident from Table 3 that the prediction of $7Q_2$ for the Central region is good, but unsatisfactory for the Southeastern region. When both the Central and Southeastern regions are combined, the prediction is considered to be only fair. The prediction accuracy of $7Q_{20}$ is unsatisfactory for all the regions.

3. Index Method: The test results (N.S.R.^{2}) for the Central, Southeastern and Combined Regions indicate that the index method may be an appropriate prediction method for 7Q2 and $7Q_{20}$ for the Central region but does not seem to be a satisfactory prediction tool for $7Q_2$ flows in the Southeastern region. Although the number of test stations in the Southeastern region is fewer than the Central region, combining the two regions together did not improve the prediction accuracy for the Combined Region over the Southeastern region.

4. Mapped Isolines Method: The $7Q_2$ unit low flows from these maps were estimated for the Central and Southeastern regions by interpolating the values between the contour lines. The $7Q_{20}$ low flows were estimated by multiplying the estimated $7Q_2$ using the $7Q_{20}/7Q_2$ ratio determined from Figure 2. It is evident from Table 3 that the method of mapped isolines of unit low flows for the Central, Southeastern and the Combined regions appears to be a robust technique which generally tended to give the most acceptable prediction results.

DISCUSSION OF THE RESULTS

A comparison of the observed and the estimated $7Q_{20}$ low flows for the Combined region for all the methods is presented in Figure 3.

Table 3(a): The Nash-Sutcliffe, R^2!, for Testing the Estimation Techniques *

Method/ Low Flows	Central Region	Southeastern Region	Combined Region
Regression Method			
Group II (Fifth Set)			
7q20	0.24	-11.65	-1.22
7q2	0.64	-5.91	-0.04
Group III			
7q20	0.72	-15.49	(a) -2.13 (b) -7.14
7q2	0.71	-6.32	(a) -0.21 (b) -0.95
Group IV			
7q20	0.73	-6.09	(a) -0.76 (b) -0.56
7q2	0.71	-3.32	(a) -0.25 (b) -0.01
Group V			
7q20	0.40	-0.51	0.08
7q2	0.28	-0.66	0.11
Group VI			
7q20	0.67	-11.32	-2.49
7q2	0.68	-7.35	-0.50
Index Method			
7q20	0.82	-0.29	-0.67
7q2	0.83	-5.46	-0.38
Area Proration Method			
7q20	0.02	-0.63	-0.01
7q2	0.96	-0.14	0.83
Mapped Isolines Method			
7q20	0.53	0.72	0.71
7q2	0.95	0.66	0.92

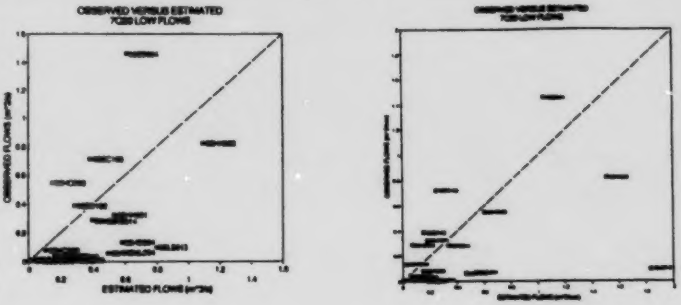
* includes stations 02KC014 and 02LB013

! N.S.R^2=1 represents perfect prediction

Table 3(b): The Nash-Sutcliffe, R^2, for Testing the Estimation Techniques **

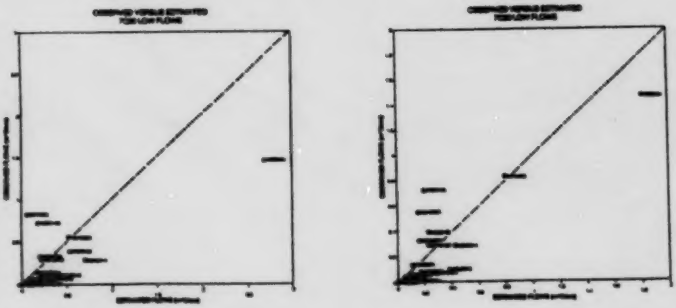
Method/ Low Flows	Central Region	Southeastern Region	Combined Region
Regression Method			
Group II (Fifth Set)			
7q20	0.24	-0.57	0.03
7q2	0.64	0.01	0.47
Group III			
7q20	0.72	-0.57	(a) 0.00 (b)-2.97
7q2	0.71	0.62	(a) 0.70 (b) 0.29
Group IV			
7q20	0.73	-0.32	(a) 0.34 (b) 0.34
7q2	0.71	0.18	(a) 0.49 (b) 0.50
Group V			
7q20	0.40	0.70	0.27
7q2	0.28	-0.42	0.13
Group VI			
7q20	0.67	-1.10	-0.10
7q2	0.68	-0.39	0.44
Index Method			
7q20	0.82	0.92	0.44
7q2	0.83	-0.12	0.45
Area Proration Method			
7q20	0.02	-0.18	0.04
7q2	0.96	0.12	0.86
Mapped Isolines Method			
7q20	0.53	0.73	0.75
7q2	0.95	0.89	0.95

** excludes stations 02KC014 and 02LB01 3 due to effects of regulation



REGRESSION (NSR^2 0·34)

INDEX (NSR^2 0·44)



AREA PRORATION (NSR^2 0·04)

MAPPED ISOLINES (NSR^2 0·75)

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TEST STATIONS OBSERVED Vs
ESTIMATED
7 Q 20 COMBINED REGIONS

FIGURE . 3

The prediction techniques which were developed equal or exceed the accuracy of the methods identified in the literature review.

In general it was found that for estimation of low flows in the Central region, any one of the methods (i.e. index, regression or mapped isoline) can be used satisfactorily. However, for the Southeastern (and hence for the Combined regions), the method of mapped isolines was found to be the most consistent for satisfactory estimation of low flows. Refinement of the regression technique for watersheds in the Southeastern region appears to require additional investigation including definition and incorporation of other watershed parameters in order to sufficiently explain low flow characteristics.

RECOMMENDATIONS FOR FUTURE STUDY

It is recommended that similar low flow prediction techniques be developed for other regions of Ontario. Further investigation should also be undertaken for watersheds located in the Southeastern region to develop appropriate watershed parameters for refining low flow estimates.

ACKNOWLEDGEMENT

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B6

RETRACTABLE COMPOSITE ABSORBENTS FOR ENVIRONMENTAL CLEAN-UP.

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INTRODUCTION

Chemical spills into lakes and rivers constitute a source of contamination to the water supply. Some of these chemicals sink to the sediments and eventually dissolve into the water. The immobilization and clean-up of chemical spills is required to minimise dissolution of the contaminant to the water. In the previous project (#375C), a crosslinked polymer absorbent was developed that is capable of removing a range of chemicals from water. In Project #456C, the retractable absorbent was tested under field conditions. The results of this field trial will be presented.

CROSSLINKED POLYMER ABSORBENT

Upon exposure to a chlorinated solvent, crosslinked ethylene vinyl acetate (EVA) will absorb the solvent and swell. Absorption continues until the polymer cannot expand any further due to the crosslinked nature of the absorbent.

Pilot scale production of crosslinked EVA beads was carried out using an EcoPlastics custom built reactor, a stainless steel vessel containing a rotating ribbon. EVA beads and hexane, containing the desired amount of dissolved initiator lauroyl peroxide, were added to the reactor and the beads were soaked for one hour in a controlled nitrogen atmosphere. The reactor was flushed again with nitrogen for an hour, and then heated to 60°C. The beads were heated at this temperature until the initiator had undergone several half-lives, approximately 27 hours.

Lab scale evaluation of the crosslinked EVA beads showed that they had absorption capacities in the range of 20 g tetrachloroethylene/g polymer, had good structural integrity after absorption of the chemical, showed a low rate of release of absorbed chemicals into the water stream, and were easily placed and retrieved from a simulated river bed without detectable loss of the absorbed solvent.

FIELD TRIAL

SITE

In order to demonstrate the effectiveness of the technology, a field trial was conducted. The site chosen was that of the 1985 spill of tetrachloroethylene in the St. Clair River. The initial spill of 11,000 L was recovered, but small pools are still seen. A grid system was set up over the 50 m x 50 m clean-up area to monitor the appearance of any pools of tetrachloroethylene. There is very little material currently present. During an annual quarterly inspection in the Spring of 1990, around 2 L of a dark brown liquid were collected. This liquid mixture contained tetrachloroethylene and carbon tetrachloride in an approximate ratio of 7:3.

The river bottom is generally flat and sandy. In the Fall of 1989, the area was disturbed to install a collection system for any solvent pools that might accumulate. Trenches were dug and most of the area was backfilled with coarse gravel.

ABSORBENT MATS

The absorbent beads were sewn into mats (500 g absorbent/mat). The mats were designed to withstand the rigorous conditions that could be expected on the river bottom. The 2 ft x 2 ft mats were made of a vinyl coated fibreglass screen, with holes of around 1.5 mm x 2.5 mm which would allow any chemical spill material to pass through into contact with the absorbent material within the mats.

A diver recorded the location of pools of solvent on the river bottom. The size of most of these pools ranged from "dime" size to "quarter" size. The smallest pools were tiny beads, and the largest pool was around 4 inches x 2 inches. The diver returned to some of those areas with the mats and staked them into the sediment. A total of eight mats were staked down. Two of the mats were placed in control areas where no solvent pools were observed, one at the upstream boundary of the grid study site, and one in the middle of the study site.

After 20 days, the mats were retrieved from the river bottom. Upon retrieval, the diver noted that the mats had been covered with a dusting of sediment, which was a half an inch thick in some places.

After the stakes were removed, each mat was placed in its own 6 mil thick polyethylene bag, most of the water was squeezed out, then the bag was sealed. Each mat was therefore protected from cross-contamination. The bags containing the mats were brought to the surface and placed in drums for transportation to Eco Corp. Research Centre for analysis.

ANALYSIS OF THE ABSORBENT RETRIEVED FROM THE ST. CLAIR RIVER BOTTOM

GENERAL COMMENTS

The mats that were placed in the areas where pools were observed had a distinct odour of chlorinated solvents. Some of the beads within these mats were coloured dark brown indicating absorption of the chemical pools. These dark beads were in patches, indicating that the pools that had made contact with the beads were absorbed. Other beads in these mats ranged in colour from light brown to light gold. The mats that were not placed directly over observed pools had an odour of algal growth. These beads also had a slight yellow colour.

MASS OF MATERIAL RETRIEVED

The mass of liquid absorbed by the polymer beads was measured as follows. The beads were removed from each mat, washed in tap water to remove any sand, patted dry on paper towels, then weighed. The weight of crosslinked beads (500 g) which had been similarly soaked in water, washed and dried was subtracted from the weight of beads from each mat obtained above. The resulting masses of material within the beads is shown in Table 1. The total mass of solvent material retrieved is around 218 g.

Table 1. Mass of material in the absorbent beads retrieved from the St. Clair River bottom, after washing the beads and patting them dry.

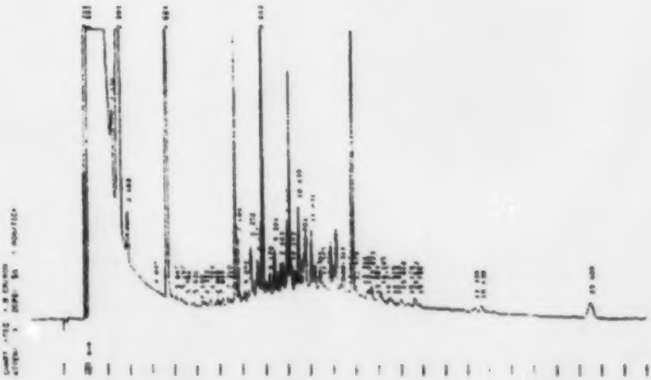
Sample Mat		Mass of Absorbed Material In Beads (g)
ECO-101	Pools observed	14
ECO-102	Pools observed	46
ECO-103	Pools observed	21
ECO-104	Pools observed	63
ECO-105	Pools observed	28
ECO-106	Pools observed	25
ECO-107	No pools observed	13
ECO-108	No pools observed	8

IDENTIFICATION OF MATERIAL ABSORBED

Samples of the beads were extracted in methylene chloride and analyzed by gas chromatography using a flame ionization detector. Figure 1 shows the existence of many other significant peaks besides that from tetrachloroethylene. Under these conditions, tetrachloroethylene has a residence time of 4.66 min. The methylene chloride gives rise to the large peak at 1.09 min., and an impurity in the methylene chloride gives a peak at 2.5 min.

At the time of writing, analysis of the retrieved material has not been completed. However, it appears that the polymer will absorb many other trace compounds.

Figure 1. Chromatogram of a methylene chloride extract of the
beads retrieved from the river bottom.
Column type: DB-1, 0.32 mm ID, 30 m long
Temperature program: 70°C for 3 min.,
20 °C/min. to 220°C,
isothermal for 15 min.
Carrier gas: He, 6.5 mL/min.



ABSORPTION OF TRACE AMOUNTS OF CHEMICALS FROM WATER

Tetrachloroethylene was observed in the methylene chloride extracts of the beads from all of the mats. Methylene chloride extracts from the beads of mats placed in areas where no pools of chemicals were observed showed the presence of trace amounts of tetrachloroethylene. This indicates that the beads will also act as an absorbent of trace amounts of chemicals dissolved in water or in the sediment.

The ability of crosslinked EVA to pick up tetrachloroethylene from solution without direct contact with the bulk phase was confirmed in laboratory studies. Beads placed in water containing dissolved tetrachloroethylene were removed and dried, then extracted in methylene chloride. The methylene chloride extracts were analyzed by gas chromatography and showed the presence of tetrachloroethylene.

SUMMARY

The crosslinked absorbent placed in screen mats performed as expected. In areas where pools of solvent were observed, the bulk solvent was absorbed if direct contact was made with the mat. Some trace amounts of tetrachloroethylene were absorbed from the water or sediment by all of the mats. Although there was very little pooled material visibly present on the river bottom (less than 2 L had accumulated over a four month period), the polymer absorbent in the mats collected around 200 g of this material over the twenty day period of the trial. The mats, which covered around 0.12 % of the 50 m x 50 m study site picked up around 6 % of the 2 L of material recovered by vacuuming.

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80

ADVANCED TECHNOLOGY FOR DESTRUCTION OF ORGANIC POLLUTANTS IN WATER STREAMS

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INTRODUCTION

The environment is contaminated on a global level with a variety of toxic pollutants that come to the environment from various sources. The level of these pollutants (mostly organic) has now increased to the point that immediate and innovative action is needed to address the problem.

Conventional pollution treatment technologies, such as carbon adsorption, air stripping and bio-oxidation, are effective in removing many organic pollutants from water streams, but they exhibit a major drawback. Both carbon adsorption and air stripping merely transfer the organic pollutants from one medium to the other. Biological treatment, on the other hand, is relatively slow and inefficient in removing many man-made organic pollutants such as chlorinated hydrocarbons. An efficient technology is required, which will not only remove the organic pollutants from the water streams, but also destroy them.

Among advanced photo-oxidation processes, the TiO_2 photocatalysed removal of organic pollutants has recently begun to show considerable promise (1 - 4). The TiO_2 photocatalytic degradation of various organic compounds by illuminated TiO_2 is very well documented in literature (see for instance references 5 - 13). The illumination of TiO_2 in water with light of wavelength <400 nm generates excess electrons in the conduction band (e^-_{CB}) and positive holes (h^+_{VB}) in the valence band (Figure 1).

$$TiO_2 + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \qquad (1)$$

At the surface the holes either react with adsorbed H_2O or surface OH^- groups to form ·OH radicals.

$$h^{+}_{VB} + H_2O(ads.) \text{ --------> } \cdot OH + H^{+} \quad (2a)$$

$$h^{+}_{VB} + OH^{-}(sur.) \text{ --------> } \cdot OH \quad (2b)$$

Excess electrons in the conduction band probably react with molecular oxygen to form superoxide ions

$$e^{-}_{CB} + O_2 \text{ --------> } O_2^{\cdot -} \quad (3)$$

which can further disproportionate to form more $\cdot OH$ radicals.

$$2O_2^{\cdot -} + 2H_2O \text{ --------> } 2\cdot OH + 2OH^{-} + O_2 \quad (4)$$

The $\cdot OH$ radicals are extremely reactive and readily attack organic molecules, eventually degrading them to CO_2 and H_2O (and halide ions when the organic molecule contains halogen atoms). Thus the advantage of this technology is that it not only removes, but also destroys organic pollutants.

EXPERIMENTAL SECTION

The patented Nulite photoreactor (14) comprises a jacket, a lamp and a photocatalytic sleeve. The lamp emits ultraviolet light in the 300 - 400 nm range and is mounted coaxially within the jacket. Around the lamp lies a sleeve formed of fibreglass mesh that is coated with titanium dioxide (anatase). The anatase is activated by ultraviolet light. Contaminated water flows through the reactor in parallel with the lamp. Typically, 4 L of contaminated water was circulated through the system for 15 min in the dark. At this point the light was switched on and analysed on a Hewlett Packard 5890A gas chromatograph using a megabore DB-5 (30 m long, 0.53 mm in diameter) with an electron capture detector operating at 300 °C and nitrogen (14 mL/min) was used as carrier gas.

RESULTS AND DISCUSSION

The major practical problem in using TiO_2 as a photocatalyst is the "hole-electron" recombination process. This process is efficient and considered as the principal energy wasting step in the TiO_2 photocatalytic degradation of organic pollutants. The low quantum yield (< 5%) of the TiO_2 photocatalytic degradation of organic compounds is indicative of the effect of the "hole-electron" recombination process.

A challenging opportunity does exist to improve the degradation rate of organic pollutants by preventing the "hole-electron" recombination process. This is an important step prior to commercial application of the TiO_2 technology for water treatment.

One attractive strategy for inhibiting the "hole-electron" recombination process is to add efficient (preferably irreversible) electron acceptors to the reaction. In order for these additives to efficiently inhibit the recombination process they should fulfil the following criteria: (a) readily accept the superoxide ions ($O_2^{\cdot -}$), (b) rapidly dissociate into harmless products and (c) provide additional routes for the formation of $\cdot OH$ radicals or other powerful oxidizing agents. We have examined four additives: oxygen, hydrogen peroxide, ozone and ammonium persulphate and have found the results very promising.

I. Effect of Oxygen

The presence of oxygen proves essential for the TiO_2 photocatalytic degradation of organic compounds to be efficient. Figure 2 shows, for comparison, the degradation of 2,4-dichlorophenol under nitrogen, oxygen and our usual air atmosphere (no gas added) conditions. It is evident that when nitrogen was introduced the degradation rate decreased remarkably. However, introducing oxygen led to an 80% increase in the degradation rate of 2,4-DCP. Similar results were obtained when air was introduced in the line just before the reactor. Evidently, oxygen traps the conduction band electron to form superoxide ions ($O_2^{\cdot-}$) and thus prolongs the lifetime of the photogenerated "hole" which is necessary for $^{\cdot}OH$ radical production. The superoxide ions could disproportionate as in equation (4) to form further $^{\cdot}OH$ hydroxyl radicals.

II. Effect of Hydrogen Peroxide

The simplest process available for the generation of hydroxyl radicals is the direct photochemical cleavage of hydrogen peroxide. However, this process is usually associated with serious practical problems. The exceptionally low molar extinction coefficient of hydrogen peroxide, and the necessity of using expensive UV light (200-300 nm) are obvious problems. The efficiency of the process is very susceptible to high levels of suspended solids and other light absorbing substances present in water.

Our approach is not to irradiate H_2O_2 directly, but instead to use H_2O_2 as an irreversible electron acceptor. On accepting an electron, either from the conduction band or the superoxide ion, hydrogen peroxide decomposes according to the following equations (15):

$$H_2O_2 + e^-_{cb} \longrightarrow {}^{\cdot}OH + OH^- \qquad (5a)$$

$$H_2O_2 + O_2^{\cdot-} \longrightarrow {}^{\cdot}OH + OH^- + O_2 \qquad (5b)$$

Obviously, this will not only prolong the lifetime of the valence band "hole" as previously discussed, but it will also provide an additional route for $^{\cdot}OH$ radical formation. We have examined the effect of H_2O_2 on the degradation of a mixture of organic pollutants containing *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and

2,4,6-trichlorophenol (10 ppm each). Figure 3 illustrates the degradation of these components as a function of irradiation time in the absence and presence of H_2O_2. Clearly our results show that H_2O_2 markedly increases the degradation rates of all the components involved in this mixture.

iii. Effect of Ozone

Ozone is currently used in some industrial advanced photo-oxidation processes. In these processes ozone is directly irradiated by UV light, as is the case with H_2O_2, therefore we have chosen to use ozone as an irreversible electron acceptor.

The formation of ozonide ion ($O_3^{\cdot -}$) through electron transfer from the conduction band of the TiO_2 to ozone, has been established for some time (16) although no attempt has been made to use ozone as an irreversible electron acceptor in the TiO_2 photocatalytic degradation of organic compounds in aqueous solutions. In fact, $O_3^{\cdot -}$ can also be formed by electron transfer from the superoxide ion to ozone.

$$O_3 + e^-_{cb} \longrightarrow O_3^{\cdot -} \qquad (6a)$$

$$O_3 + O_2^{\cdot -} \longrightarrow O_3^{\cdot -} + O_2 \qquad (6b)$$

The ozonide ion in water reacts with a proton to form $^{\cdot}OH$ radicals.

$$O_3^{\cdot -} + H^+ \longrightarrow {}^{\cdot}OH + O_2 \qquad (7)$$

Thus, the addition of ozone to the TiO_2 photocatalytic process is expected to provide more $^{\cdot}OH$ radicals.

Recently we independently examined the TiO_2 photocatalytic degradation of 2,4-dichlorophenol and nitrobenzene in the presence and absence of ozone, and have found that ozone markedly increased the photodegradation rates of these compounds. Control experiments showed that ozone in the dark (no light in the reactor) also degrades these compounds, although at a lower rate than those experiments where light is present in the photoreactor. We should mention that under our conditions, ozone does not absorb the light since our lamps have very little output below 300 nm.

iv. Effect of Ammonium Persulphate

In many industrial wastes, where degradation of organic pollutants is the major concern, the addition of an inorganic anion (such as persulphate ion) to enhance the degradation rate of the organic pollutants may be justified. In homogeneous reactions the persulphate ion dissociates, on accepting an electron, to a sulphate ion and a sulphate radical ion (17).

$$S_2O_8^{2-} + e^- \longrightarrow SO_4^{-\cdot} + SO_4^{2-} \qquad (8)$$

Based on this experimental fact, we have chosen ammonium persulphate as an electron acceptor in the photocatalytic degradation of organic pollutants with the hope that, under our conditions, $S_2O_8^{-\cdot}$ could also accept an electron from the conduction band or the superoxide ion $(O_2^{\cdot -})$ to give SO_4^{2-} and $SO_4^{-\cdot}$

The sulphate radical ion is effective in two ways: (a) it can act as a precursor for $^{\cdot}OH$ radicals as shown in the following equation:

$$SO_4^{-\cdot} + H_2O \longrightarrow SO_4^{2-} + {}^{\cdot}OH + H^+ \qquad (9)$$

and (b) it could act as a powerful oxidizing agent for organic pollutants.

We have examined the degradation of a mixture of *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol (10 ppm each) in the presence and absence of persulphate ions. The results presented in Figure 4 show clearly that $S_2O_8^{2-}$ markedly increased the degradation rates of the four components involved in the reaction mixture.

CONCLUSIONS

Our results clearly indicate that the TiO_2 photocatalytic degradation of organic pollutants by the Nulite reactor opens a good opportunity for water treatment. The TiO_2 process will offer a clean, inexpensive and simple technology to remove organic pollutants from water streams.

ACKNOWLEDGEMENTS

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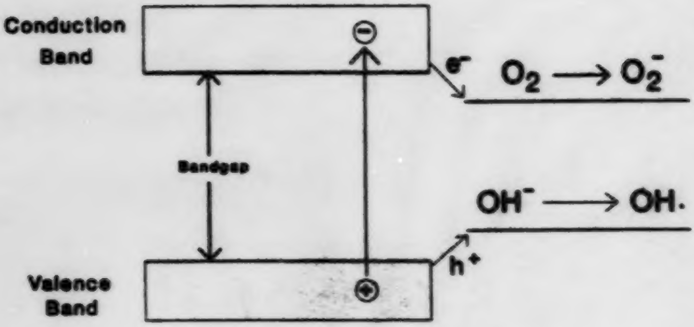
Conduction Band
Bandgap
Valence Band
e^-
h^+
$O_2 \longrightarrow O_2^-$
$OH^- \longrightarrow OH\cdot$

Figure 1: Reduction of oxygen by the conduction band electron and oxidation of hydroxyl group by the valence band hole.

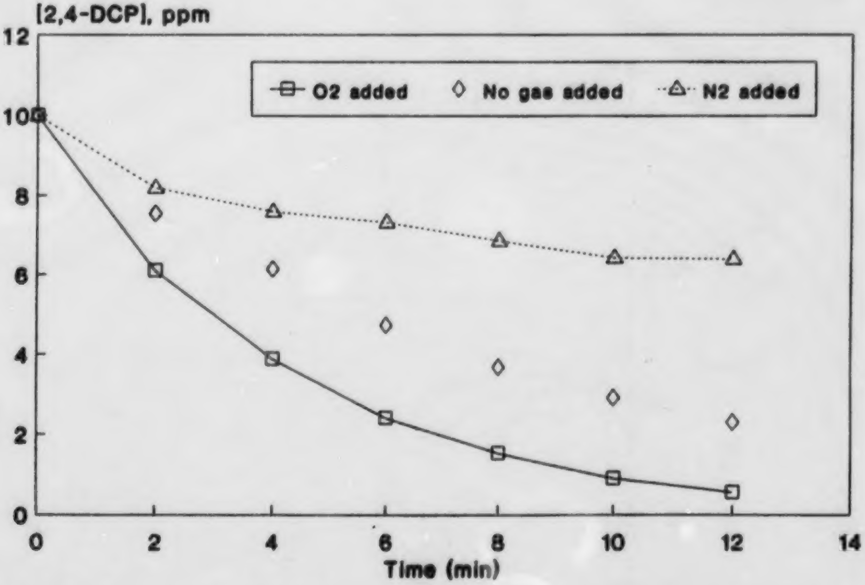

Figure 2: The photocatalytic degradation of 2,4-dichlorophenol in open system (no gas added), under nitrogen and under oxygen.

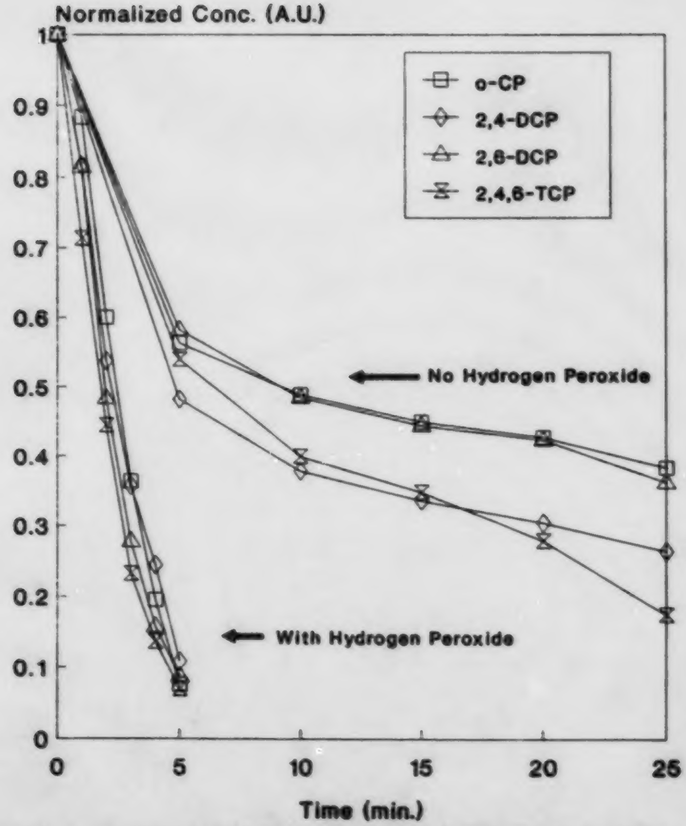

Figure 2: The photocatalytic degradation of a mixture of four chlorinated phenols (10 ppm each) in the presence and absence of hydrogen peroxide.

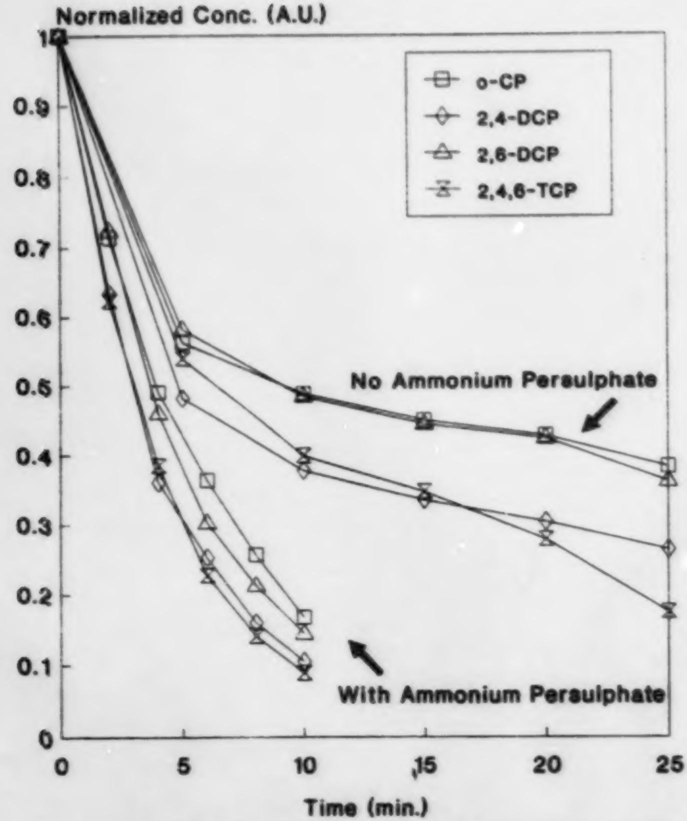

Figure 4: The photocatalytic degradation of a mixture of four chlorinated phenols (10 ppm each) in the presence and absence of ammonium persulphate.

CARCINOGENICITY TESTING OF BLEACHED KRAFT MILL EFFLUENT USING IN VIVO RAINBOW TROUT ASSAYS

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ABSTRACT

In vivo assays with rainbow trout are being used to determine whether bleached kraft mill effluent (BKME) is carcinogenic to fish. BKME extracts were prepared by column chromatography with XAD resins. Non-polar to medium polarity compounds were extracted using XAD-4 resin, and polar compounds were extracted using XAD-7 resin. Ames-positive mutagens are present in the XAD-7 extract, and the XAD-4 extract induces elevated aryl hydrocarbon hydroxylase activity and peroxisome proliferation activity in hepatocytes after intraperitoneal injection into rainbow trout. In vivo experiments are in progress to determine whether BKME extracts are carcinogenic to rainbow trout, or act as promotional agents in the development of aflatoxin B_1-induced tumours.

INTRODUCTION

Bleached kraft mill effluents (BKME) have been shown to have mutagenic activity (1, 2), and to induce physiological disturbances in fish, including induction of cytochrome P450 dependent-monooxygenases (3, 4). In addition, white sucker populations in close proximity to bleached kraft pulp mills have been reported to have a high prevalence of liver tumours and "liver disease" (5). In this study, in vivo bioassays with rainbow trout are being used to identify the toxic and carcinogenic effects of BKME to fish.

Extracts of BKME were prepared with XAD macroreticular resins. Non-polar to medium polarity compounds were extracted with XAD-4 resin, and polar compounds were extracted with XAD-7 resin. These extracts were injected intraperitoneally into rainbow trout in both short-term and long-term bioassays to determine carcinogenic activity, promotional activity, ability to induce cytochrome P450-dependent aryl hydrocarbon hydroxylase (AHH) activity in hepatocytes, and ability to induce proliferation of peroxisomes in hepatocytes. The latter toxic response (peroxisome proliferation) is thought to be involved in a carcinogenic process which does not involve genotoxicity and requires chronic exposure to the carcinogenic agent (6, 7).

It is anticipated that these studies will aid in determining whether BKME are carcinogenic to fish. These data will also identify the classes of compounds which are responsible for the toxic/carcinogenic/genotoxic activity of BKME.

METHODS

Preparation of Extracts:

BKME were obtained as "grab" samples from the Canadian Pacific Forest Products kraft mill in Thunder Bay, Ontario. BKME were filtered in aliquots of 2 L through a 0.3 µm glass fibre filter (GFC). The GFC was extracted into methanol in a soxhlet apparatus. The filtrate was divided into 2 aliquots. One aliquot was passed through Amberlite XAD-4 resin, and non-polar to medium polarity compounds adsorbed to this resin were eluted with 100 mL of diethyl ether. The other aliquot was passed through Amberlite XAD-7 resin, and polar compounds adsorbed to the resin were eluted with 100 mL of methanol. All extracts were concentrated by rotary evaporation and made up to a final volume in acetone. Thus, 3 extracts were produced from each effluent sample: i) Filter extract, ii) XAD-4 extract, and iii) XAD-7 extract. Extracts were diluted with appropriate carrier solvents, and doses for in vitro and in vivo assays were calculated in terms of "mL equivalents" of the original effluent volume.

Carcinogenicity Assay:

Rainbow trout (Oncorhynchus mykiss) were injected with test chemicals and extracts in the sac fry stage using the methods described by Metcalfe et al. (8), or trout eggs were immersed in solutions of test chemicals according to the aqueous immersion protocol described by Hendricks (9). In some treatments, early life stages of trout were exposed to two test treatments by both of these methods. At 2 additional points during the development of the fish (at 2 mo and 5 mo), some of the trout were injected intraperitoneally with test extracts, using the methods described by Kotsanis and Metcalfe (10). Table 1 lists the treatments and numbers of dosed animals remaining in the trout carcinogenicity assays currently underway. The promotional activity of XAD-4 extract is being assayed after initiation with the potent fish hepatocarcinogen, aflatoxin B_1.

Mutagenicity Assay:

Effluent extracts were tested for mutagenic activity with the Ames fluctuation assay (11), using Salmonella typhimurium tester strains TA100 and TA98, with and without exogenous activation with rat S-9. Extracts were tested at doses between 25 and 200 mL equivalents per test well.

Assay for AHH Induction:

Rainbow trout (3 fish per treatment) weighing approximately 300 g were anesthetized with quinaldine sulfate and injected intraperitoneally with 4 doses (0.8, 8, 80 and 160 mL equivalents/kg) of each of the effluent extracts, or carrier solutions (negative control), or β-napthoflavone (positive control) at a dose of 100 mg/kg. After dosing, the fish were placed in water at 12°C for 72 h.

At 72 h post-dosing, the fish were sacrificed with an overdose of MS-222. The livers were removed and placed in cold 1.15% KCl. The livers were homogenized and a microsomal solution prepared according to the method described by Guengerich (12). The microsomal preparation was stored in liquid nitrogen until AHH activity was assayed. The AHH activity was determined by the method described by Nebert and Gelboin (13). Activity was expressed as fluorescence units per mg of protein per minute of incubation. Protein content of the microsomal preparation was determined using the method described by Bradford (14).

Assay for Peroxisome Proliferation:

Rainbow trout (3 fish per treatment) weighing approximately 100 g were injected as described for the AHH assay with 3 doses (16, 80, 160 mL equivalents/Kg) of each of the effluent extracts, or carrier solutions (negative control), or di-(2-ethylhexyl)phthalate (positive control) at doses of 2, 1 and 0.2 g/kg. Fish were subsequently placed in water at 12°C for 5 days.

At 5 days post-dosing, fish were sacrificed as described above, and small pieces of liver tissue were fixed in cold 2.5% glutaraldehyde/0.1 M cacodylate buffer (pH 7.4) for 3-6 h. The tissues were then washed for 2 to 4 h in 0.1 M cacodylate buffer and incubated at 37°C for 30 to 60 min in diamino-benzidine (DAB) medium, according to the method described by Novikoff and Goldfischer (15). After DAB incubation, the tissues were post-fixed with osmium tetroxide, embedded in Epon, sectioned with an ultramicrotome, and examined by transmission electron microscopy (TEM) for evidence of proliferation of cellular peroxisomes in hepatocytes. Alternatively, thick sections (1-5 μm) of Epon-embedded tissues were prepared, stained with toluidine blue (16), and examined for evidence of peroxisomal proliferation by light microscopy (x1500 magnification).

RESULTS AND DISCUSSION

The XAD-7 and XAD-4 extracts of bleached kraft mill effluent gave different biological responses. However, filter extracts gave no response in the in vitro assay for mutagenicity, or the in vivo assays for induction of AHH activity and peroxisome proliferation.

Mutagenicity, as determined in the Ames fluctuation assay, was primarily confined to the XAD-7 extract containing relatively polar compounds (Table 2), although there was a slight response in tests with a high dose of XAD-4 extract. Therefore, as has been reported for other kraft mill effluents (1, 2), the majority of mutagenic activity in these effluents is confined to a fraction containing water-soluble compounds. Mutagenic activity was only seen in tests with the TA100 tester strain, both with and without addition of rat S-9. Thus, the mutagenic constituents of the XAD-7 extract are direct-acting mutagens that produce base-pair substitutions in bacterial DNA. However, mutagenicity was not observed when XAD-7 extract was tested at similar doses in the Ames plate incorporation assay. This observation indicates that mutagenic compounds in the effluent extract are relatively labile, as has been noted in other studies (1).

The data summarized in Figure 1 indicates that AHH activity was elevated above background levels by both XAD-4 and XAD-7 extracts, but induction data at the highest doses of effluent extracts (160 mL equivalents/kg) indicate that compounds in the XAD-4 extract are the most potent inducers of hepatic AHH activity. Thus, relatively non-polar compounds are responsible for this biological response. Although it has been reported previously that in situ exposure of fish to BKME elevates levels of hepatic cytochrome P450-dependent monooxygenases (3, 4), the active compounds in BKME have not previously been characterized according to chemical polarity. In the future, we will test the effluent extracts for ability to induce hepatic 7-ethoxyresorufin-o-deethylase (EROD) activity in rainbow trout; a monooxygenase reponse which is reportedly elevated more dramatically after BKME exposure than the AHH response (3, 4). The induction of cytochrome P450-dependent monooxygenases in fish exposed to BKME is significant because induction of these hepatic enzymes may alter the metabolism of other carcinogenic substances, or chronic induction of these MFO enzymes may have a promotional effect upon tumour development.

Induction of proliferation of cellular peroxisomes by certain classes of chemicals, including phthalate plasticizers, has been correlated with the development of hepatic tumours in rodent models (6, 7). Tumourigenesis generally requires chronic dosing with chemicals. It also appears that the mechanism of carcinogenesis with "peroxisome proliferators" does not involve genotoxicity, as is the case with "classic" carcinogens. It is possible that BKME may be carcinogenic to fish as a result of chronic exposure to peroxisome proliferator substances, rather than genotoxic chemicals.

As summarized in Table 3, the highest dose of the XAD-4 extract induced the formation of cytoplasmic organelles in hepatocytes, which resemble peroxisomes in size and staining characteristics. These organelles were visible by TEM and light microscopy, and they resembled the organelles induced by the positive control compound, DEHP. Similar responses were not observed in the XAD-7 treatments or the filter extract treatments, although there was evidence of hepatocellular necrosis in the XAD-7 treatments. In addition to the induction of peroxisome-like organelles in the XAD-4 treatment (high dose), increased amounts of smooth ER were also visible in the hepatocytes of these fish. This response, which has also been noted in rodents exposed to peroxisome proliferators (17), may be correlated with increased cytochrome P450-dependent monooxygenases in the liver. Studies are continuing on this response to BKME, including analysis of trout hepatic catalase activity, which is also correlated with peroxisome proliferation (18).

The carcinogenicity bioassay for trout exposed to BKME extracts is in the 7th mo of a scheduled 10 mo duration. At the end of the assay, fish will be sacrificed and liver tissues will be prepared for a histopathological survey of tumour incidence in the various treatments. Other tissues will be examined grossly for evidence of tumour development, and, if necessary, prepared for histological confirmation of malignancy.

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Ian Smith of the OME Rexdale Laboratory provided technical advice on the AHH and EROD assays and expedited sampling of kraft mill effluents. Dave Rokosh of the Rexdale Laboratory provided data on the Ames fluctuation assay of effluent extracts. D. Murray of the OME District Office at Thunder Bay arranged for collection of effluent samples.

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Table 1: Summary of treatments in the rainbow trout carcinogenicity assay of BKME.

TREATMENT		NUMBER REMAINING (7 Mo)
Egg/Fry Exposure	I.P. Injection	
AFB1[1]	-	120
AFB1[1] plus XAD-4[2]	-	114
AFB1[1] plus XAD-4[2]	XAD-4[3]	96
XAD-7[4]	-	118
XAD-7[4] plus XAD-4[2]	-	113
XAD-7[4] plus XAD-4[2]	XAD-4[3]	93
XAD-4[2]	-	111
XAD-4[2]	XAD-4[3]	85

1) Trout eggs exposed by aqueous immersion to a solution of aflatoxin B_1, at a concentration of 0.25 µg/mL for 1 h.

2) Trout sac fry exposed by microinjection of extract (0.5 µl volume) at a dose of 0.05 mL equivalents per sac fry.

3) Trout juveniles exposed by i.p. injection at 2 mo and 5 mo to the extract, at a dose of 500 mL equivalents/kg.

4) Trout eggs exposed by aqueous immersion to a solution of XAD-7 extract, at a concentration of 3.4 mL equivalents/mL for 8 h.

Table 2: Mutagenic response to BKME extracts in the Ames fluctuation assay. Effluent samples were tested with *Salmonella* strains TA98 and TA100, with and without addition of rat S-9.

EXTRACT	RESPONSE				LOWEST DOSE SHOWING RESPONSE (mL equiv.)
	TA98	TA98S[1]	TA100	TA100S[1]	
Filter	-	-	-	-	-
XAD-4	-	-	+/-[2]	+/-[2]	40
XAD-7	-	-	+	+	4.26

1) Assays run with addition of rat S-9.

2) Weak response.

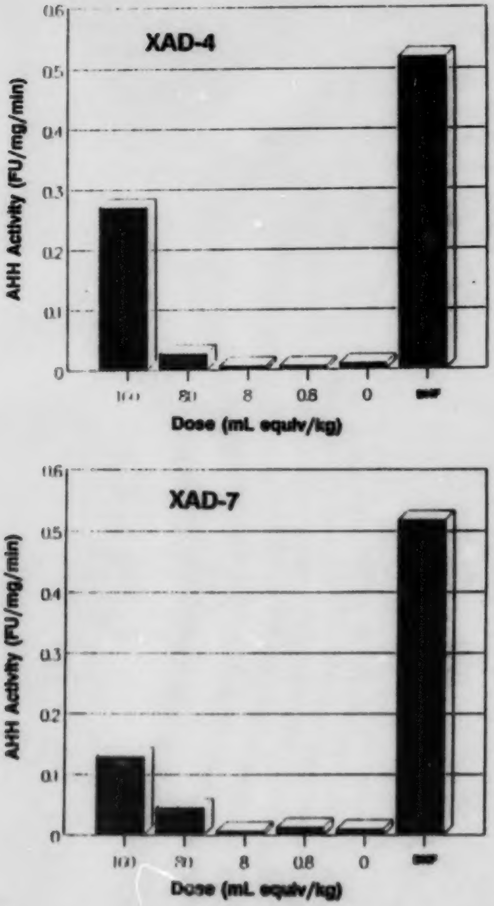

Table 2: Mean AHH activity (3 fish per dose), expressed as fluorescence units per mg protein per minute of incubation, in rainbow trout liver after exposure by i.p. injection to XAD-4 and XAD-7 extracts from BKME, or β-naphthoflavone (100 mg/kg).

Table 3: Ultrastructural (TEM) response of rainbow trout hepatocytes to exposure to BKME extracts and DEHP (positive control). Three trout were dosed per treatment.

TREATMENT	CONCENTRATION	RESPONSE
XAD-4	160 mL equiv/kg	P[1]
	80 mL equiv/kg	N[2]
	16 mL equiv/kg	N
XAD-7	160 mL equiv/kg	N
	80 mL equiv/kg	N
	16 mL equiv/kg	N
Filter	160 mL equiv/kg	-[3]
	80 mL equiv/kg	-
	16 mL equiv/kg	-
DEHP (Positive Control)	2g/kg	P
	1g/kg	P
	0.2g/kg	P
Negative Control		-

1) Proliferation of peroxisomes.

2) Evidence of necrosis among hepatocytes.

3) No response.

B12

IMPACT OF BLEACHED KRAFT MILL EFFLUENT (BKME) ON FISH POPULATIONS NEAR TERRACE BAY, ONTARIO.

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INTRODUCTION

The impact of bleached kraft pulp mills on aquatic ecosystems is a matter of international concern. Until recently, knowledge of the toxicity of pulp and paper mill effluents to aquatic life has been based primarily on laboratory toxicity tests performed under controlled conditions. Both the Canada Department of Fisheries and Oceans and the Ontario Ministry of Environment recently commissioned reviews of the impacts of pulp and paper mill effluents on aquatic life. There is a lack of knowledge of the influence of both untreated and treated whole mill effluents on the early developmental life stages of sensitive aquatic organisms, their reproduction and resistance to disease (Bonsor et al., 1988; McLeay, 1987 Colody and Sprague, 1989). Andersson et al. (1988) reported a survey of BKME impacts on perch (*Perca fluviatilis*) collected off the east coast of Sweden. Perch exposed to BKME exhibited physiological changes up to 8 to 10 km from the effluent disposal site. The major changes consisted of decreased gonad growth, increased liver size, a ten-fold increase in liver MFO activity, abnormal carbohydrate metabolism, changes in haematology and increased fin erosion. Although their investigation of physiological and biochemical impacts was extensive, the study neglected to tie the changes together and offer any mechanism to explain the impacts. The content, design and conclusions of the Scandinavian studies have been challenged (Colody and Sprague, 1989; Sprague, 1989). Our 1988 and 1989 collections parallel those of the Swedish studies (Munkittrick et al., 1989), and are the only North American results of this type to become public to date.

The primary objectives of our research were to evaluate the impact of BKME exposure on the growth and reproduction of white sucker as well as to examine relationships between changes in the endocrine system and liver MFO enzymes.

MATERIALS AND METHODS

Effluent from the pulp and paper mill at Terrace Bay, Ontario reaches Lake Superior at Jackfish Bay. Jackfish Bay is relatively isolated and provides an ideal situation to test for the impact of BKME on wild fish populations. White sucker were collected from the spawning runs in Sawmill Creek (Jackfish Bay) and the Little Gravel River (Mountain Bay), our reference site, by overnight hoop net sets in May, 1989. Fish were also collected during July and August by overnight gillnet sets in Jackfish and Mountain Bays as well as a second control site in August, Black Bay. Fork length and weight as well as the age of all fish were determined. A condition factor (k) was calculated for all fish as 100(weight/length^3). A liver somatic index was calculated as 100(liver weight/(total weight - liver weight)). A gonadosomatic index was calculated wherever possible as 100(gonad weight/(total weight - ovary weight)).

Reproductive Performance

Reproductive potential was assessed in spawning males by measuring milt volume, spermatocrit, spermatozoan motility and seminal plasma constituents. In prespawning females, reproductive potential was assessed by determining fecundity and egg size, in spawning females by determining their fertility, and in July females by estimating egg release. The effects of inherited contaminant burdens were assessed by the examination of larval responses and by cross-fertilization of gametes from exposed sites with reference gametes. Fertilized eggs were returned to the laboratory and evaluated for effects on survival, development, growth, behaviour, yolk absorption efficiency, deformation and initiation of exogenous feeding.

Relationships Between Endocrine and MFO Systems

Fish were sampled during prespawning, spawning and both summer periods for evaluation of circulating levels of steroids and liver MFO activity. Steroids were measured by radioimmunoassay by Dr. Glen Van Der Kraak using standard methods (Van Der Kraak et al., 1985; Van Der Kraak and Donaldson, 1986). MFO determinations were conducted by Ontario Ministry of Environment personnel.

In an attempt to identify the location of the impact of BKME on the endocrine system, white sucker were collected and caged in clean water. Fish received an injection of a principal gonadal steroid and circulating levels of the steroid were then to be monitored over time. This would allow assessment of pituitary function and steroid clearance rate from the blood. However, these attemps were unsuccessful due to high mortality at the control sites.

Significance to other Species

During the August sampling trip, preliminary work was completed on Lake Whitefish, which are a commercially important species in Lake Superior. Any incidental whitefish that were caught in the nets were weighed and measured. The gonads and the liver were also removed and weighed to allow site comparisons.

RESULTS

During all collections, male and female white sucker exhibited a decreased length and weight and a higher condition factor at the BKME site. This increased condition factor and an apparent increase in body fat were consistent with an increased water temperature at the BKME site, but were inconsistent with impacts on growth and reproduction. Both sexes exhibited a decreased growth rate and a shift in size distribution towards smaller fish.

Ripe male white sucker collected during the spring of 1989 showed decreased sperm motility, but no differences in milt volume, spermatocrit, or seminal plasma constituents (Na, K, Cl, osmolality). Female fish had a decreased egg size, a decreased GSI among older fish, and a decreased fecundity in younger fish. Egg size at the BKME site did not increase with age. There were no apparent differences in fertilization rates or in the females ability to release eggs between sites. Studies on eggs returned to the laboratory showed no differences in larval survival, development, behavior, or initiaion of exogenous feeding. However, the larvae do appear to grow at a slightly slower rate at the BKME site. During the August collections, male fish showed no secondary sexual characteristics (tubercles). All mature males examined in August at four other sites showed significant tubercle development.

Testosterone levels were significantly reduced in both prespawning and spawning females at the BKME site. Testosterone, 11-ketotestosterone and 17α,20β-dihydroxyprogesterone levels were significantly reduced in exposed males during the prespawning and spawning periods. July samples showed no differences in female steroid levels, but males showed reduced levels of testosterone and 11-ketotestosterone. August samples showed reduced testosterone in both females and males relative to two reference sites, as well as reduced 11-ketotestosterone levels in males and reduced 17β-estradiol levels in females.

The MFO analysis determined the activity of benzo(a)pyrene (BaP) hydroxylase (aryl hydrocarbon hydroxylase activity, AHH) towards diphenyloxazole (PPO) and BaP. Spawning male white sucker showed a 2- to 3-fold increase in activity for both BaP and PPO substrates. Spawning females did not show increased activity relative to the reference sites. Summer collected white sucker showed a 6- to 18-fold increase in activity towards PPO, and 5-fold increase in BaP activity. There was no significant difference in UDPGT activity (glucuronosyl transferase activity towards p-nitrophenol) in the summer samples. The steroid injections attempted in August were unsuccessful. However, when BKME exposed fish were removed to clean water for a period of four days, there was a significant reduction in MFO activity (both PPO and BaP) when compared to the BKME site.

Preliminary work on the whitefish that were collected from under the plume, revealed marked elevations in body fat, decreased gonadal size and increased liver weight relative to those at two reference sites. A large number of the BKME fish showed no evidence of gonadal maturation two months prior to the spawning season.

DISCUSSION

Although condition factor increased at the BKME site, there was no concomitant increase in growth rate, suggesting that factors associated with energy allocation have been affected. Factors which might affect energy allocation include liver damage and/or decreased food availability. In females, the decreased growth rate and fecundity are characteristic of a population experiencing problems with food availability (Munkittrick and Dixon, 1989). However, white sucker show an increased condition factor. The combination of increased condition factor, decreased growth (length at age), and decreased fecundity observed at the BKME site appears paradoxical. Fish which cannot obtain sufficient energy for either growth or reproduction would be expected to show a lower condition factor. These results are consistent with the hypothesis of impacts of increased MFO activity on carbohydrate metabolism.

White sucker usually show an increase in egg size as they get older, as was noted at the reference site in this study. However, egg size did not increase with age at Jackfish. This was also noted in a previous study associated with the absence of the growth of mature fish (Munkittrick and Dixon, 1988), but at Jackfish the white sucker are continuing to grow, although at a decreased rate. The relative decrease in egg size of older fish results in a relative decrease in gonad weight, without a change in absolute fecundity. However, younger females at the Jackfish site show a decreased fecundity relative to the reference site. The correlations of fecundity changes with younger fish instead of older fish, and the increased condition factor at BKME sites suggests that the impact of BKME is not on food availability, but on the ability of the fish to convert the energy into growth or reproduction. These changes, along with the decreased gonadal size in males and the absence of secondary sexual characteristics, suggests that there are major abnormalities in the reproductive cycle. The decrease in steroid levels found throughout the year at the BKME site support this hypothesis. Despite the lower steroid levels (as much as 50% reduced), and the reduction in gonadal size, these fish still appear to spawn successfully as there were no differences in fertilization rate of the eggs, or survival, development, behavior, and initiation of exogenous feeding in the larvae.

One of the functions of the MFO system is to hydroxylate multi-ring carbon compounds to increase their solubility and facilitate their excretion. It has been suggested that the increased MFO activity associated with BKME exposure might affect circulating levels of hormonal steroids (Jonsson et al., 1976; Thomas, 1988), which have a multi-carbon ring nucleus, and are essential for the control of reproduction. The decreased steroid levels in our study also appear to be associated with the increase in MFO activity. We felt that these increased MFO activities were reducing the circulating levels of steroids in the blood. However, we were unsuccessful in our attempt to display this link between increased MFO activity and decreased steroid levels due to our inability in keeping caged suckers alive. However, when looked at on an individual basis, there was not a significant regression between MFO activity and steroid levels at the BKME site. For example, the fish with the highest induced MFO activity did not correspond to the fish with the lowest steroid levels. From these results, it becomes obvious that more work is needed before the critical links between BKME exposure, increased MFO activity and impacts on reproduction can be made.

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S13

INVOLVEMENT OF BILE DUCT DISEASE AND LOSS OF RESISTANCE TO CHEMICAL CARCINOGENS IN THE PATHOGENESIS OF LIVER NEOPLASMS IN BENTHIC FISH FROM LAKE ONTARIO

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ABSTRACT

The relationship between hepatic neoplasia and concurrent parasitic liver disease was examined in white suckers from polluted regions of western Lake Ontario. Fluke *(Sanguinicola sp)* and nematode (Spirurida) liver infestation resulted in inflammation, fibrosis, bile duct proliferation, and subsequent biliary obstruction and cholestasis. Adult male white suckers with segmentally obstructed livers, identified by exploratory laparotomy, were orally administered ^{3}H-benzo(a)pyrene (^{3}H-BaP) (70 Ci/mmol; 2.5 mCi/fish). Cytosolic glutathione S-transferase (GST) activity (CDNB conjugation) in obstructed liver was approximately 50% of normal surrounding liver. Covalent binding of ^{3}H-BaP to hepatic protein was 1.5 fold greater in obstructed liver compared to corresponding normal liver. The formation of BaP-DNA adducts was minimal in both obstructed and normal liver (5 fmol/mg DNA), however one obstructed lobe had significantly higher levels of adducts (120 fmol/mg). The primary bile acid chenodeoxycholic acid (CDCA) represented 23% of total bile acids extracted from cholestatic liver and 5% of total in normal liver when analyzed by HPLC. Oral administration of CDCA (50 mg/fish) in white suckers resulted in a 33% decrease in cytosolic GST activity. CDCA inhibited cytosolic GST activity in vitro in a dose-related manner (I_{50}=100μM CDCA). Cholestasis resulting from parasitic liver disease alters the bile acid composition of white suckers resulting in a significant elevation in CDCA. CDCA is a potent inhibitor of GST, an important enzyme involved in the detoxification of PAHs in white suckers. Concurrent hepatic disease may increase the susceptibility of white suckers to hepatocarcinogenesis by reducing constitutive resistance to carcinogenic PAHs.

INTRODUCTION

Epidemiological evidence indicates that a complex interplay of etiologic and pathologic factors may be responsible for the development of liver cancer in many species (Harris and Sun, 1984; DeFlora et al., 1989; Lee et al., 1990;). Hepatocellular carcinoma (HCC) frequently coexists in conditions of dynamic hepatic disease in which inflammation, hepatocellular necrosis, proliferation and cirrhosis are commonly observed. In man, chronic liver disease, caused by a variety of parasitic (schistosomiasis, clonorchiasis, opisthorchiasis), viral (hepatitis B virus infection) and toxic (alcoholism, aflatoxicosis) agents is commonly associated with primary hepatocellular carcinoma (HCC) in high prevalence regionc (sub-Saharan Africa and the Far East) (Nakashima et al 1975; Kew and Popper, 1984).

In western Lake Ontario, white suckers exposed to chemical carcinogens in contaminated sediment develop liver cancer that is frequently associated with inflammatory and proliferative liver disease, bile duct obstruction and cholestasis (Hayes et al., 1990). The association between concurrent liver disease and the development of liver neoplasms in white suckers indicates a multifactorial carcinogenic process involving chemical carcinogens as only one causative factor. We have attempted to characterize the mechanistic basis of multifactorial hepatocarcinogenesis in white suckers, to determine how concurrent liver disease might make these fish susceptible to environmental carcinogens such as polycyclic aromatic hydrocarbons (PAH).

Cholestasis is known to produce profound changes in bile acid metabolism which, in turn, may induce alternate pathways of xenobiotic metabolism. For example, GSTs have dual functions in the liver ie catabolism of xenobiotics and a binding/carrier function for endogenous substances that are not substrates (ie bilirubin and bile salts). Numerous experimental studies have demonstrated that, by acting as non-substrate ligands, high intracellular concentrations of bile acids have a strong inhibitory effect on GST activity (Boyer and Vessey, 1987; Singh et al., 1988; Boyer et al., 1984; Hayes and Mantle, 1986; Vessey and Zakim, 1981). Our previous studies have demonstrated that glutathione conjugation is an important means of detoxifying PAHs to which white suckers are exposed (Kirby et al., 1990). Concurrent cholangiohepatitis and cholestasis may render these fish more susceptible to PAHs by altering normal bile acid metabolism and inhibiting constitutive detoxification enzymes such as GST. In this study we have examined the effect of segmental cholestasis and bile acid accumulation on the metabolism and toxicity of BaP in white suckers.

MATERIALS AND METHODS

Materials.

Hydroxyapatite (DNA grade, Bio-Gel HTP) was obtained brom Bio-Rad Laboratories (Mississauga, Ont.). ^{3}H-BaP (specific activity 70 Ci/mmol was purchased from New England Nuclear (Boston, MA). Chenodeoxycholic acid (99% purity), deoxyribonuclease 1, alkaline phosphatase type III (EC 3.1.3.1) and phosphodiesterase I (EC 3.1.4.1) were purchased from Sigma Chemical Company (St. Louis, MO.)

Treatment of animals

Male white suckers (n=241) were caught from the Humber River (Toronto, Ontario) and Keefer's Creek (Owen Sound, Ont.) during their spring spawning migrations and were maintained for 1 week in laboratory holding tanks in clean well water. Laparotomies were performed on all fish under anesthetic (2-phenoxyethanol, 5ml/liter water) to examine for the presence of segmental liver obstructions. Fish were orally administered ^{3}H-BaP (70 Ci/mmol; 2.5 mCi/fish) and were killed 18 hours later. Obstructed and normal liver was separated and frozen for further analysis. In a separate experiment, CDCA (50 mg/fish) was administered by gavage followed in 2 hours by oral dosages of ^{3}H-BaP (2.5 mCi/fish). Fish were killed 18 hours later and liver samples were removed and frozen. Obstructed and normal liver was removed from untreated fish for preparation of cytosol and bile acid extraction.

Isolation of DNA and preparation of BaP-DNA adducts

BaP-modified DNA was isolated from normal and obstructed liver tissue by hydroxylapatite chromatography according to the method described by Adriaensens et al. (1984). Briefly, tissues were homogenized in 0.16 M sodium phosphate containing 8 M urea (MUP) with EDTA, centrifuged and washed with ethyl acetate and diethyl ether. Following nitrogen evaporation of the organic solvents the aqueous layer was applied to hydroxylapatite columns (5 cm X 30 cm) and residual proteins and RNA were eluted with 0.24 MUP. After elution of urea with 0.48 M phosphate buffer, the DNA was eluted with 0.48 M phosphate buffer and was concentrated and dialysed against 10 mM Tris-HCl/MgCl$_2$ buffer (pH 7.1) in an Amicon model 52 concentrator apparatus with a YM10 membrane. The DNA was then precipitated with 2 volumes of ethanol, redissolved in 1 ml 10 mM Tris-HCl/MgCl$_2$ and quantified by 260 nm absorbance . BaP-modified DNA was hydrolyzed to deoxyribonucleosides according to a method described by Alexandrov et al (1988). DNA (1 mg/ml buffer) was dissolved in 10 mM Tris-HCl/MgCl$_2$ buffer (pH 7.1) containing 10 mM MgCl and was enzymatically digested to nucleosides using DNase I (400 units/mg DNA) for 8 hours; phosphodiesterase (0.06 units/mg DNA) for 48 hours and finally alkaline phosphatase (2.5 units/mg DNA) for 24 hours. Nucleosides bound to DNA were separated from free nucleosides by applying samples to Sep-Pak C18 cartridges, washing unbound nucleosides with 30% methanol and eluting BaP-nucleoside adducts with 80% methanol. Radioactivity was then assessed by LSC and expressed as fmol/mg DNA.

Protein isolation and quantification of BaP covalently bound to protein

Protein was isolated from the CIP extract obtained during the isolation of DNA as described by Stowers and Anderson (1984). Briefly, 1 ml aliquots of each CIP extract were shaken, centrifuged and the protein was then exhaustively washed with methanol, ethyl acetate and finally 90% methanol until counts were at background levels. Pellets were dissolved in 2 ml 0.5 N NaOH and radioactivity was analysed by liquid scintillation chromatography and expressed per unit protein.

Extraction and HPLC analysis of bile acids

Bile acids were extracted from obstructed and normal liver tissue according to a method developed by Kinugasa et al, 1981. Briefly, whole liver pooled from obstructed and normal lobes were homogenized in 2 volumes of distilled water and lyophilized. Samples (1g) were then extracted overnight in 100 ml ethanol containing 0.1% ammonia. The extracts were evaporated to dryness, dissolved in 70% methanol and neutral lipids were removed twice with n-hexane. The 70% methanol layer was then evaporated to dryness, dissolved in distilled water and aqueous components were removed by loading the sample onto Sep-Pak C18 cartridges, washing with distilled water, and eluting bile acids in methanol for HPLC analysis. Individual bile acids were separated by reverse phase HPLC on a C18 column (Biorad Hipore RP-318; 250 x 4.6 mm) with a continuous gradient flow of 40 mM ammonium phosphate buffer (solvent A) and acetonitrile (solvent B) (initial 35% A; 65% B, final 40%A; 60% B) in thirty minutes at a flow rate of 1.25 ml/min. Individual bile acids were detected by UV absorbance (210 nm) and were identified by bile acid standards in methanol and quantified by integration of peak areas.

Chenodeoxycholic acid inhibition of GST activity

Samples of liver were homogenized in 0.25 M cold sucrose (containing 5 mM HEPES, pH 7.0). Cytosol was prepared as the final supernatant of centrifugation at 10,000g (30 min, 4°C) and 100,000 g (60 min 4°C). Cytosolic GST activity was determined with 1-chloro-2,4-dinitrobenzene (CDNB) as substrate (pH 6.5, 25°C) by the method of Habig *et al*., (1974). Protein concentrations in cytosol were determined by the Biorad protein assay. The inhibitory effect of chenodeoxycholate on the GST-mediated conjugation of glutathione to CDNB was measured by preincubating the sample with five different concentrations (100, 200, 300, 400 and 500 mM) of the inhibitor for 30 minutes prior to administration of the substrate. Because of the limited solubility of chenodeoxycholate, 1.25% (v/v) methanol was included in each assay, including controls.

RESULTS

Segmental liver obstructions were visible as caudal liver lobes discolored dark green with retained bile pigments in 14% of male white suckers from the polluted site (Humber R.) (Table 1). No obstructions were visible grossly in reference fish. Tumors were visible grossly as focal areas of discoloration (tan brown color) or as large raised neoplasms frequently within or in close assocation to obstructed lobes. Histologically, there was periportal fibrosis, necrosis of bile duct epithelium, infiltration of melanomacrophages and other inflammatory cells, retention of bile pigments, and bile duct proliferation within these obstructed areas (Fig. 1). Trematodes *(Sanguincola sp.)* and nematodes (Spirurida) were visible within bile ducts and migrating through liver parenchyma. (Fig.1). Foci of hepatocellular and cholangiocellular alteration and advanced neoplasms (cholangiocellular and hepatocellular carcinoma were frequently adjacent to areas of bile duct inflammation and fibrosis (Fig. 2).

Cytosolic GST activity in segmentally obstructed cholestatic lobes was 63% of the GST activity normal liver. BaP-deoxyribonucleoside adducts and BaP adducted to hepatic protein was higher in obstructed liver compared to normal liver (Table 2, Fig. 4). HPLC analysis of extracted bile acids revealed that the primary bile acid chenodeoxycholic acid (CDCA) was elevated approximately 6 fold in cholestatic liver (Fig. 5) in comparison to normal (Fig. 6) and represented 23 mole % of total bile acids (Table 3).

Hepatic cytosolic GST activity in suckers treated orally with chenodexycholic acid was 66% the GST activity of control fish (Fig 7.). The inhibition of hepatic cytosolic GST by CDCA in vitro was dose-related in µmolar concentrations (I_{50}=100 µM).

DISCUSSION

This study indicates that concurrent hepatic diease in white suckers is associated with a reduction in constitutive resistance to carcinogenic PAHs. In spite of the correlation between HCC and hepatic disease, there is little experimental evidence concerning the cellular and molecular mechanisms involved in hepatocarcinogenesis (Gu, 1988). While it is well recognized that neoplasia is a consequence of persistent hepatocellular proliferation, it is equally conceivable that altered xenobiotic metabolism in hepatitis and cirrhosis increases the susceptibility of hepatocytes that are normally resistant to chemical hepatocarcinogens. For example, recent studies indicate that stimulation of carcinogen metabolism in hepatitis B virus-infected woodchucks may be an important factor in the synergism of viral hepatitis and HCC.

During cholestasis, the intracellular concentration of organic ions such as bile acids increase to levels which significantly impair the catalytic activity of GST (Greim et al., 1972; Boyer and Vessey, 1987). This suggests that cholestatic liver may be unusually susceptible to injury by toxic electrophiles detoxified by GST. Cholestasis in several species, including humans, usually results in a reduction in secondary and tertiary bile acids and a shift towards increased primary bile acids such as cholic acid and chenodeoxycholic acid (Oelberg and Lester, 1986; Palmer R.H., 1972; Kinugasa et al., 1981; Greim et al., 1972; Greim and Popper, 1971; Greim et al., 1972). The bile acid composition of white suckers in this study closely resembles that of rainbow trout (Denton and Yousef, 1974). For example, CDCA comprises approximately 5% of total bile acids of normal adult fish of both species. The increase in CDCA (24% of total bile acids) in cholestasic liver of white suckers has also been observed in rats with bile duct ligation (Kinugasa et al., 1981; Greim et al., 1972; Greim and Popper, 1971) and severe chronic biliary obstruction in humans (Greim et al., 1972). Concentrations of CDCA less than 100 μM, levels that correspond to intrahepatic concentrations during cholestasis, (Greim et al., 1972) are strongly inhibitory for most rat hepatic GST isoenzymes in vitro (Hayes and Mantle., 1986). Because GSH conjugation diminishes the binding of PAH epoxide metabolites to DNA (Hesse et al., 1982; Hesse et al., 1990; Jernstrom et al., 1982; Ketterer, 1988), a reduction in GST activity may increase the susceptibility of DNA to electrophilic attack. Therefore, the inhibition of GST by CDCA both in vivo and in vitro and the increased toxicity of BaP in obstructed liver suggests that the altered bile acid compositon in cholestatic liver may reduce GST-mediated resistance to PAHs in white suckers.

It is interesting to speculate on possible mechanisms that might explain the differences in susceptibility of these fish and other species to hepatocarcinogenesis. Differences in susceptibility to hepatocarcinogenesis may indeed be related to liver disease and changes in bile acid metabolism. For example, experimental studies have demonstrated a promotional effect of bile duct obstruction and various bile acids in hepatocarcinogenesis (Kinami et al., 1990; Blair et al., 1990; Kitazawa S. et al., 1990; Cameron R.G. et al., 1982; Tsuda et al., 1984; Tsuda et al., 1988). Furthermore, experimentally-induced postnecrotic cirrhosis (Watanabe et al., 1987; Newberne et al., 1966) and fluke infestation (Thamavit et al., 1987; Thamavit et al., 1988) are important promoting factors in chemical hepatocarcinogenesis. Others have suggested that the relationship of bile acids to liver tumor development may be due to intrinsic mutagenic/initiating activity of bile acids, (Kitazawa et al., 1990), metabolic formation of carcinogenic metabolites from bile acids (Cook and Hasslewood, 1934), and hepatocellular injury due to detergent effects of bile acids (Greim et al., 1972).

The phenomenon of parasite-induced liver disease and the relationship to hepatic neoplasia in white suckers may be contextual and related to environmental conditions. For example, sanguinicolids are usually found in blood vessels (ie. mesenteric arteries) of fresh water fish with lodging of eggs terminally in gill lamellae. It is unusual for adult sanguinicolids to migrate to the liver and even rarer for adults to be found within bile ducts. It is possible that this anomalous trematode migration is due to heavy infestations resulting from conditions associated with polluted environments that may influenceß the life cycle of Sanguinicola sp. (ie. higher concentrations of snail intermediate hosts). The fact that relatively few flukes were extracted from obstructed liver may be due to seasonal fluctuations in sanguinicolid infestation a hypothesis that is supported by extraction of immature forms in this study. However, the inflammatory reaction within the liver is likely an immune response to deposited eggs and totally unrelated to the mechanical presence of adults. Similarly, the presence of the spirurid nematode within the liver (tentatively identified as Acuraridoidea) is also considered unusual. Interestingly, the definitive host of acuarids is usually a piscivorous bird, such as gulls, which are becoming increasingly prevalent in industrialized areas. It is likely, therefore, that the hepatic disease concurrent with liver neoplasia is a species specific phenomen in white suckers (eg. species specific parasites, liver anatomy etc) and not readily extrapolated to humans. Nevertheless, parallels may be drawn in similar situations in humans where loss of constitutive resistance (ie. elderly patients, chronic alcoholism, hereditary anomalies of xenobiotic metabolism) increases the susceptibility to liver neoplasia.

The low liver tumor incidence in white suckers exposed to high sediment levels of PAHs (Hayes et al., 1990), the detoxification of reactive intermediate metabolites of PAHs by GSTs (Kirby et al., 1990) and the low levels of BaP-DNA adducts observed in this study suggest that these fish are normally quite resistant to the carcinogenic effects PAHs. Alterations to the mechanisms that provide this carcinogenic resistance (ie. reduction in GST activity) may explain any increase in susceptibility. The coincidence of liver disease and hepatic neoplasia and the reduced detoxification of carcinogens associated with cholestasis in these fish suggest that there is a strong association between the consequences of hepatic disease and loss of resistance to PAHs in white suckers.

TABLES

Table1. Prevalence of segmental liver obstructions in white suckers from polluted and reference sites.

Site	Number of fish	Number with segmental obstructions	% of total
Humber R.[1]	241	33	13.6
Keeler's Cr.[2]	36	0	0

[1] Toronto, Ont., polluted site

[2] Owen Sound, Ont., reference site

Table 2. Quantification of BaP-deoxyribonucleoside and BaP protein adducts in cholestatic and normal liver from white suckers.

	BaP-DNA adducts (fmol/mg DNA)				BaP-protein adducts (fmol/mg protein)			
	fish no.				fish no.			
Type of liver	1	2	3	4	1	2	3	4
normal	2.7	20.5	6.3	2.3	3	12	8	6
cholestatic	133.3	1.1	1.7	0.5	20	13	4	4

Table 3. Comparison of distribution of chenodeoxycholic acid in cholestatic and normal liver from white suckers

Bile Acids	Normal liver	Obstructed liver
Total bile acid pool (mmol/g tissue)	2.5	2.9
CDCA (µmol/g tissue)	120	690
CDCA (mole % total)	5	23

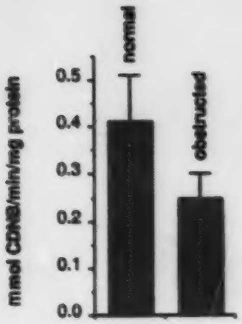

Fig 3. Cytosol GST activity in cholestatic and normal liver of tissue white suckers

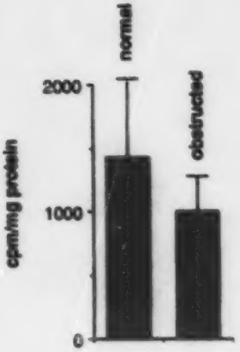

Fig 4. Covalent binding of ^{3}H-BaP to hepatic protein in cholestatic and normal liver of white suckers

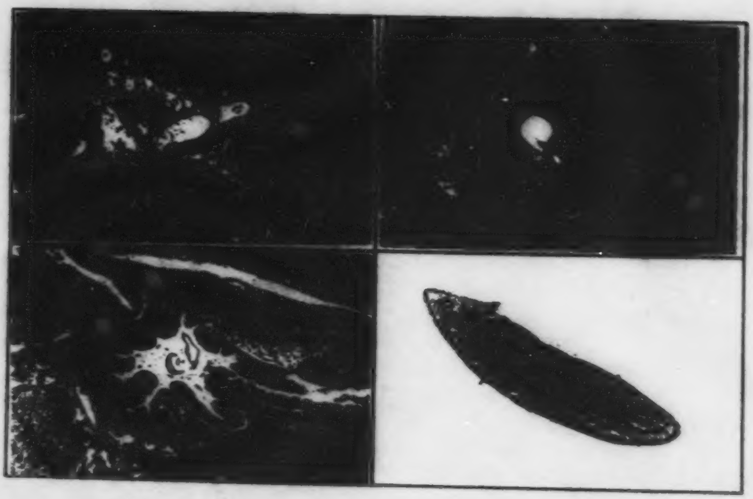

Fig. 1. Parasitic bile duct disease in white sucker liver. a, Cholangiohepatitis, periportal fibrosis and bile duct proliferation. b, Proliferative bile ducts. c, *Sanguinicola sp.* present in major bile duct with periductal fibrosis. d, *Sanguinicola sp.* extracted from obstructed liver lobe.

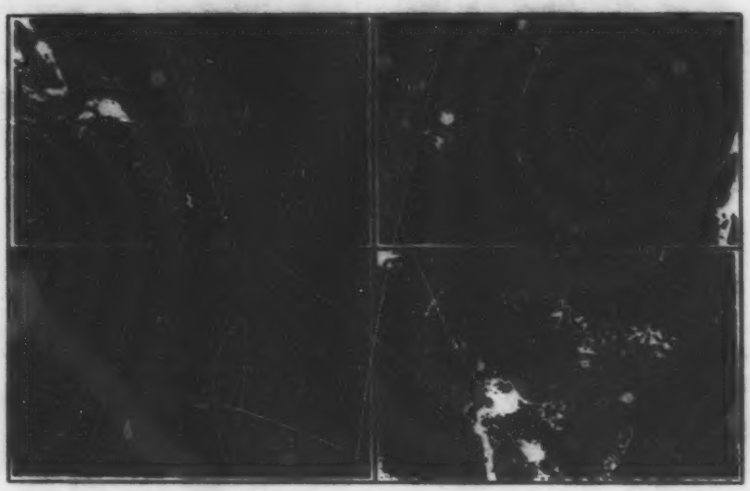

Fig. 2. Hepatic neoplasia in association with bile duct disease. a, Focus of hepatocellular alteration and bile duct inflammation. b, Cholangioma with adjacent parasitic granulomas. c, Hepatocellular carcinoma and d, cholangiocellular carcinoma adjacent to areas of bile duct fibrosis and proliferation.

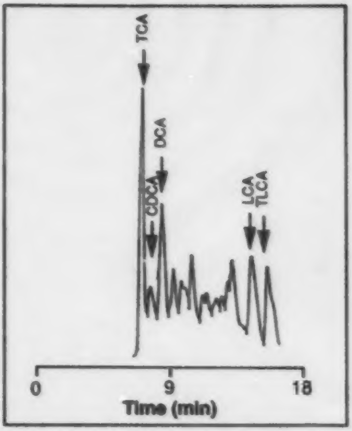

Fig.5. Chromatogram of bile acids extracted from normal liver

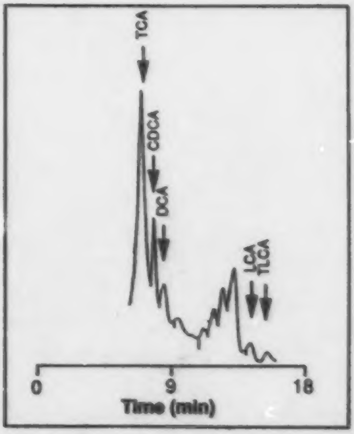

Fig. 6. Chromatogram of bile acids extracted from obstructed liver showing increase in CDCA.

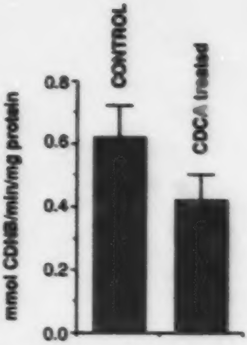

Fig. 7. Hepatic cytosolic GST activity in suckers treated orally with chenodeoxycholic acid and controls.

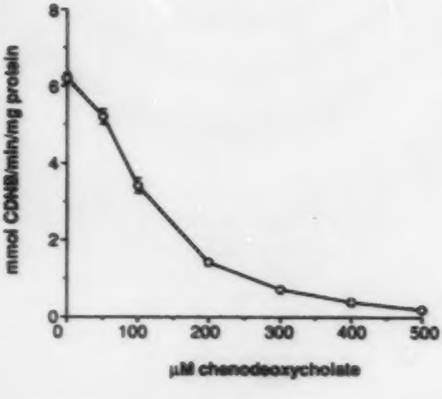

Fig. 8. Inhibition of sucker hepatic cytosolic GST by chenodeoxycholic acid in vitro.

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B14

The use of Benthic invertebrates in mapping toxic areas of sediment and determining the efficacy of sediment cleanup operations

by

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Abstract

Chironomids are representatives of a widely distributed group of insects known as midges. Chironomids from 4 locations in the Niagara River Watershed were sampled and classified as either normal or deformed. Among the 230 chironomids taken from the contaminated site in 1988, 14% (32) possessed menta with gross deformities. Following the replacement of the contaminated sediments at this site with clean sediments, the frequency of menta abnormalities fell to 7% (n=176). The frequency of abnormalities at the upstream "control" site ranged between 2 and 11%. We concluded that the sediments in the "cleanup" area had been decontaminated and that in the absence of the coal tar contaminants (e.g. PAH's) the frequency of larval chironomid abnormalities declined to well within the background levels observed at the upstream control site.

Nickel, chromium, zinc and lead were 60 to 500 times more concentrated in the sediments downstream of the Atlas Specialty Steels Co. than they were in the sediments of the upper Welland River or in the Chippawa Creek. These metals reached concentrations of 4,900 mg kg^{-1} dry weight (ppm) of nickel versus 10 ppm upstream, 890 versus 5 ppm lead, 1,050 versus 30 ppm zinc and 5,120 verses 10 ppm chromium. Twenty five percent of the chironomids removed from the heavy metal contaminated sediments downstream of the Atlas Specialty Steels Co. Ltd. displayed gross mentum abnormalities. Further downstream, below the Welland Sewage Treatment Plant, the frequency of abnormalities fell to 17 %. Both of these sites displayed significantly more deformed chironomids than at the control site ($P < 0.01$).

INTRODUCTION

Deformities of Benthic Invertebrates Exposed to Teratogens

Aquatic communities are logical places to study the impact of mutagens and teratogens. As a result, many ecologists have attempted to use invertebrate deformities to indicate the presence of genotoxins in aquatic sediments (Hamilton and Saether, 1971; Wiederholm, 1984; Warwick et al., 1987; Warwick, 1985 and Dickman et al. 1991). Research that was carried out on the frequency of deformities of chironomid larvae in polluted freshwater sediments led to the use of abnormalites in their mouth parts (menta), and antennae as a correlate with the presence of genotoxic contaminants (Hamilton and Saether, 1971; Wiederholm, 1984; Warwick et al., 1987 and Lan et al. 1990).

The most widely distributed benthic invertebrates in freshwater are Chironomid larvae. These larvae represent one of the more sensitive stages in the Chironomid life cycle. Chironomid larvae have symmetrical mouth parts (menta). Deformed specimens are characterized by menta which are asymmetrical. Hamilton and Saether (1971) also considered unusual thickening of the chironomid larval body wall as a deformity. These researchers have also suggested that different types of deformities may be induced by different types of pollutants. For example, certain types of chemicals are associated with an unusually high frequency of deformed antennae (Warwick et al. 1987), while other chemicals are associated with an unusually high frequency of deformed mouth parts (Dickman et al. 1990). This susceptibility to various pollutants appears to also differ among distinct chironomid species (Wiederholm, 1984). Warwick et al. (1987) also found that some chironomid species are far more sensitive to mutagens than are other species.

Tradescantia

Tradescantia, more commonly known as Spiderwort, is a perennial herbaceous plant that can be affected by radiation and certain chemical mutagens (Cebulska-Wasilewska et. al, 1981). It is a plant that readily propagates asexually and one that flowers continuously throughout the year. *Tradescantia* is quite suitable for both laboratory and in situ studies and as a result it is a commonly utilized scientific subject (Ichikawa, 1981).

Tests that most commonly employ the Spiderwort include two mutagenicity assays; the stamen hair assay and the micronucleus assay. The stamen hair assay focuses on detecting all pink or clear mutant cells from the string of violet coloured cells that are normally present (Ichikawa, 1981). The micronucleus test is based on the principle that chromosome breakage caused by mutagens in the early meiotic pollen mother cells of *Tradescantia* occur as small additional nuclei (micronuclei or MCN). These MCN are revealed in the cells of tetrads which are the end products of meiosis (Te-Hsiu, et al., 1983).

Objectives of this Study

The purpose of this study was to determine whether the sediment clean up operation at a site on the Niagara River (Chippawa) had resulted in a statistically significant reduction in the number of chironomid abnormalities occurring at the site prior to the clean up. The second objective of the study was to determine whether or not a positive correlation occurred between the responses of freshwater benthic invertebrates of the family Chironomidae and the angiosperm, *Tradescantia* as indicators of the presence of genotoxins in the sediments of aquatic environments. The frequency of chironomid mentum deformities and the frequency of irregular mutational events that occurred in *Tradescantia* were compared to determine whether sediments associated with a high frequency of chironomid abnormalities would also induce a high frequency of pink events and micronucleus abnormalities in *Tradescantia*.

Data were compiled from four locations within the Niagara Watershed. Two sites were located in the City of Welland along the Welland River near the Atlas Specialty Steels Co. and two sites were situated along the same river in a small town known as Chippawa. The water at the latter two sites was Niagara River water and not Welland River water (Fig. 1).

Site Descriptions

Welland River at Atlas Steels - Upstream of the Welland STP

This sample site was situated 600m downstream of the Atlas-Mansfield discharge pipe and approximately 200m upstream of a Regional Niagara Sewage Treatment Plant (STP, Fig. 2). A total of 16 dredge samples were collected at this location from May 28 to July 8, 1990. Quite often an oily film could be seen on the water's surface immediately following any disturbance of the submersed sediments. Normally, samples were taken at a distance of about 1.5m from shore and at a depth of 0.5m. Various organisms were obtained during the sorting process however, only the chironomids were examined for this report.

Welland River at Club Richelieu

Club Richelieu, located on the Welland River just downstream of the Welland sewage treatment plant (Fig. 2) was sampled throughout the summer of 1990. Sediments removed from this site were known to have elevated levels of heavy metals and oily wastes.

This site is densely colonized by cattails and other aquatic vegetation which separate the shore from the river by about 100m. A total of 12 Ponar dredge samples were taken from July 30 to August 2, 1990 from the river in front of the cattail fringe at this site. Samples were taken in the cattail colonized area approximately 10m from the river's edge and at a water depth of approximately 0.6m. During the sampling process, an oily film formed on the water's surface and the sediments taken with the Ponar dredge oozed oiled as they were examined in the sorting tray.

Upper Niagara River at the Kane Dock (Chippawa Creek)

The water at this site (Fig. 1) flows from Lake Erie by way of the Niagara River. The sample area was located in the Village of Chippawa, between 4069 and 4083 Front Street, less than 50 m downstream of the Norton Abrasives Co. discharge pipe. A total of 8 ponar dredge samples were collected at this site from June 22 to July 3, 1990.

Upper Niagara River at Kingsbridge Park (Chippawa Creek)

The water at this site (Fig. 1) also comes from Lake Erie via the Niagara River. Kingsbridge Park is located about 800m upstream of the Norton Abrasives' outfall pipe and has been characterized as a "control site" in previous studies (Dickman et al. 1990). A total of 11 Ponar dredge samples were taken at this site from July 3 to July 19, 1990, yielding an abundant collection of chironomids and a variety of other aquatic organisms.

METHODS

Benthic Invertebrates

Sampling Procedure

Sediment samples were taken using a standard 15cm X 15cm Ponar dredge at each of the four study sites. The 10 kg Ponar penetrated the sediment to a depth of about four centimeters allowing the various organisms, particularly the benthic invertebrates dwelling within this region, to be collected in a quantitative manner. At least thirty chironomid larvae were obtained from each site. This number ensured that proper statistical analyses could be carried out.

All samples were transferred from the Ponar into a bucket containing a 0.75mm mesh sieve at its base. The contents in the bucket were then sieved thoroughly to ensure that a substantial proportion of the excess dirt and clay was removed from the sample. This practice greatly facilitated the quantitative removal of the chironomids during the sorting process. Each sieved sample was placed in a glass container and labelled.

Sorting was completed within a three day period for samples that were kept refrigerated and within twenty four hours of the sampling date for those which were not. Sorting and head capsule mounting procedures are detailed in Dickman et al. (1990).

Tradescantia

This portion of the study was carried out in the lab of Dr. Mike Salamone of the Ontario Ministry of the Environment in Toronto, Ontario.

Plant cuttings were obtained from the York University greenhouse and transported to the laboratory at the Ministry of the Environment. Approximately 30 cuttings were chosen per treatment. These cuttings were suspended in the sediment or control solution through perforated aluminum covers on disposable beakers for 24 hours. This ensured that liquid absorption through the stem would take place. Following exposure, the cuttings were thoroughly rinsed three times, twice with Hoagland's Nutrient solution and once with water. This practice reduced surface mutagen residue and, consequently, the hazard of handling contaminated plants.

Plants that were exposed only to Hoagland's Nutrient solution were used to establish a base-line control value. This group was kept in a separate fume hood to prevent gaseous contamination from chemical test solutions. The standard methods of Ichikawa, (1981, stamen hairs), and Te-Hsiu, et al.(micronuclei preparations) Te-Hsiu, et al. (1983) were followed with modifications described by Salamone (unpublished MOE report).

RESULTS

Tables 1-4 summarize the results of the 51 Ponar dredge samples taken from the 4 locations along Chippawa Creek and the Welland River between May 28 and August 2, 1990. Table 5 summarizes the results of the *Tradescantia* stamen hair and micronuclei assays which were carried out using sediment from the four above mentioned sample locations.

TABLE 1
Chironomid Data
Welland River at Kingsbridge, Chippawa

Chironomid Genera	Number of ind.	Number normal chiron.		Number of grossly deformed chironomids		Number dredge samples	Density (#/m^2)	Date sampled
		#	%	#	%			
Dicrotendipes	19	18	95%	1	5%	7	121	7/3/90
Chironomus Sp.	8	7	88%	1	12%	7	51	7/3/90
Crypto-chironomus	1	1	100%	0	0%	7	6	7/3/90
C. anthracinus	5	5	100%	0	0%	7	32	7/3/90
C. semi-reducuts	2	2	100%	0	0%	0	13	7/3/90
C. semi- reductus	68	60	88%	8	12%	4	833	7/19/90
Paratendipes	4	3	75%	1	25%	4	44	7/19/90
Polypedilum	1	1	100%	0	0%	4	11	7/19/90
Procladius	2	2	100%	0	0%	4	13	7/19/90
Totals	110	99	90%	11	10%	11	698	

Total No. Species = 8, Generic Diversity = 1.07

TABLE 2 Welland River at Kane Dock, Chippawa

Chironomid Genera	Number of ind.	Number of normal chironomids		Number of deformed chironomids		Number dredge samples	Density (#/m^2)	Date Sampled
		#	%	#	%			
Chironomus Sp.	2	2	100%	0	0%	4	22	6/22/90
Cryptochironomus	1	1	100%	0	0%	4	11	6/22/90
Cryptochironomus	2	2	100%	0	0%	4	22	7/3/90
Cryptochironomus	5	5	100%	0	0%	4	55	7/8/90
Dicrotendipes	2	2	100%	0	0%	4	22	7/3/90
Dicrtotendipes	2	1	50%	1	50%	4	22	7/8/90
Endochironomus	1	1	100%	0	0%	4	11	6/22/90
Endochironomus	5	5	100%	0	0%	4	55	7/3/90
Endochironomus	7	6	86%	1	14%	4	78	7/8/90
Orthocladius	2	2	100%	0	0%	4	22	6/22/90
Paratendipes	4	4	100%	0	0%	4	44	6/22/90
Paratendipes	3	3	100%	0	0%	4	33	7/3/90
Polypedilum	1	1	100%	0	0%	4	11	6/22/90
Procladius	2	2	100%	0	0%	4	22	6/22/90
Psectrocladius	2	2	100%	0	0%	4	22	6/22/90
Psectrocladius	1	1	100%	0	0%	4	11	7/3/90
Tanytarsus	1	1	100%	0	0%	4	11	6/22/90
Tribelos jucun.	1	0	0%	1	100%	4	11	6/22/90
Totals	44	41	93%	3	7%	12	159	

Total No. of Species = 11, Generic Diversity = 2.27

TABLE 3 Chironomid Data from Welland River at Club Richelieu

Chironomid Genera	Number of ind.	Number of normal chironomids		Number of deformed chironomids		Number dredge samples	Density (#/m^2)	Date sampled
		#	%	#	%			
Chaetocladius	1	0	0%	1	100%	6	7	8/02/90
Paratanytarsus	3	3	100%	0	0%	6	22	7/30/90
Paratanytarsus	9	8	89%	1	11%	6	67	8/02/90
Phenopsectra	1	1	100%	0	0%	6	7	8/02/90
Polypedilum	1	1	100%	0	0%	6	7	8/02/90
Procladius	2	1	50%	1	50%	6	15	7/30/90
Procladius	13	11	85%	2	15%	6	96	8/02/90
Totals	30	25	83%	5	17%	12	111	

Total No. of Species = 5, Generic Diversity = 1.48

TABLE 4

Atlas Steels Chironomid Data 1990
Welland River - Upstream of the Welland Sewage Treatment Plant

Chironomid Genera	Number of ind.	Number normal chironomids		Number grossly deformed. chironomids		Number dredge samples	Density ($\#/m^2$)	Date sampled
		#	%	#	%			
Chaetocladius	1	1	100%	0	0%	4	11	5/28/90
Chironomus	1	1	100%	0	0%	4	11	5/28/90
Cladoplema	5	4	80%	1	20%	8	28	6/18/90
Cladopelma	2	1	50%	1	50%	4	22	7/08/90
Dicrotendipes	1	1	100%	0	0%	8	6	6/18/90
Paracladius	1	0	0%	1	100%	4	11	5/28/90
Paratendipes	1	0	0%	1	100%	8	6	6/18/90
Procladius	2	2	100%	0	0%	4	22	5/28/90
Tanypus	1	1	100%	0	0%	8	6	6/18/90
Tribelos	1	1	100%	0	0%	4	11	5/28/90
Totals	16	12	75%	4	25%	16	44	

Total No. of Species = 9

TABLE 5

Results 1990
Tradescantia Assays

Location of Sediment	Stamen Hair Assay	Micronucleus Assay
Kingsbridge #1	negative	negative
Kingsbridge #2	negative	negative
Welland Upstream STP #1	negative	neg/pos?
Welland Upstream STP #2	positive	neg/pos?
Garden Control	0	0
Kane Dock #1	negative	no data
Kane Dock #2	negative	negative?
Club Richelieu	negative	negative

The term "pos" is used to denote an increase over Garden Control or Kingsbridge, although the increase may not necessarily be significant.

Discussion

Kaiser and Combe (1983) described a number of types of volatile organic compounds that were found to exist in the industrial portions of the Welland River. Three of the compounds identified by Kaiser and Combe were genotoxic (Lan et al., 1990). In addition, chromium and nickel, both genotoxic heavy metals, were found at concentrations of about two orders of magnitude above background levels downstream of the Atlas Specialty Steels Co. (Dickman et al. 1991). It can be assumed therefore that the increased incidence of chironomid mentum deformities at both Club Richelieu and downstream of the Atlas Specialty Steels Co. (upstream of the Welland Sewage Treatment Plant) may be a direct result of the elevated concentrations of mutagenic heavy metal levels at these two locations.

In 1986, the Chippawa Creek, Kane Dock site was designated by the M.O.E. for a "cleanup" of its coal tar contaminated sediments. Experimental studies by Cushman (1984) indicated that pollution by a synthetic, coal tar-derived oil was correlated with a high frequency of mentum deformities in *Chironomus decorus* living in the contaminated sediments of his study ponds. We hypothesized that a cleanup of the PAH coal tar contaminated sediments in the Kane Dock area should therefore directly act to reduce the incidence of mentum deformities in chironomids sampled at this site. As indicated (Table 2), this hypothesis was supported by the fact that in 1990, 44 chironomids were removed from the cleanup site and only 7% displayed abnormalities. Before the cleanup, the frequency of abnormalities was 18% (Dickman et al. 1990). Ten percent of the 110 chironomids sampled at the control site (Table 1) displayed abnormal menta (Table 1).

Whether or not a correlation between the incidence of mentum deformities in chironomids and the mutational events that occur in *Tradescantia* exists could not be determined because, according to Dr. Salamone, the *Tradescantia* data (Table 5) were inconclusive. Although it appears as though the study site with the highest frequency of chironomid mentum abnormalities was also the site with the highest number of *Tradescantia* "pink events" additional testing with the *Tradescantia* will be needed to confirm these results.

Among the 230 chironomids taken from the contaminated site in 1988, 14% (32) possessed menta with gross deformities. Following the replacement of the contaminated sediments at this site with clean sediments, the frequency of menta abnormalities fell to 7% (n=176). The frequency of abnormalities at the upstream "control" site ranged between 2 and 11%. We concluded that the sediments in the "cleanup" area had been decontaminated and that in the absence of the coal tar contaminants (e.g. PAH's) the frequency of larval chironomid abnormalities declined to well within the background levels observed at the upstream control site.

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Figure Captions

Figure 1. The two study sites situated along the Chippawa River in Chippawa, Ontario are indicated by the arrows. The Atlas Specialty Steels and Club Richelieu sites are located near no. 4 in the Welland Industrial area. The inset indicates the location of the study area within the Great Lakes Region.

Figure 2. The two study sites situated along the Welland River in Welland, Ontario. Distances denote down stream measurements from the Atlas Specialty Steels discharge pipe. This figure was modified from a figure prepared for an MOE public document by Acres Consulting Ltd.

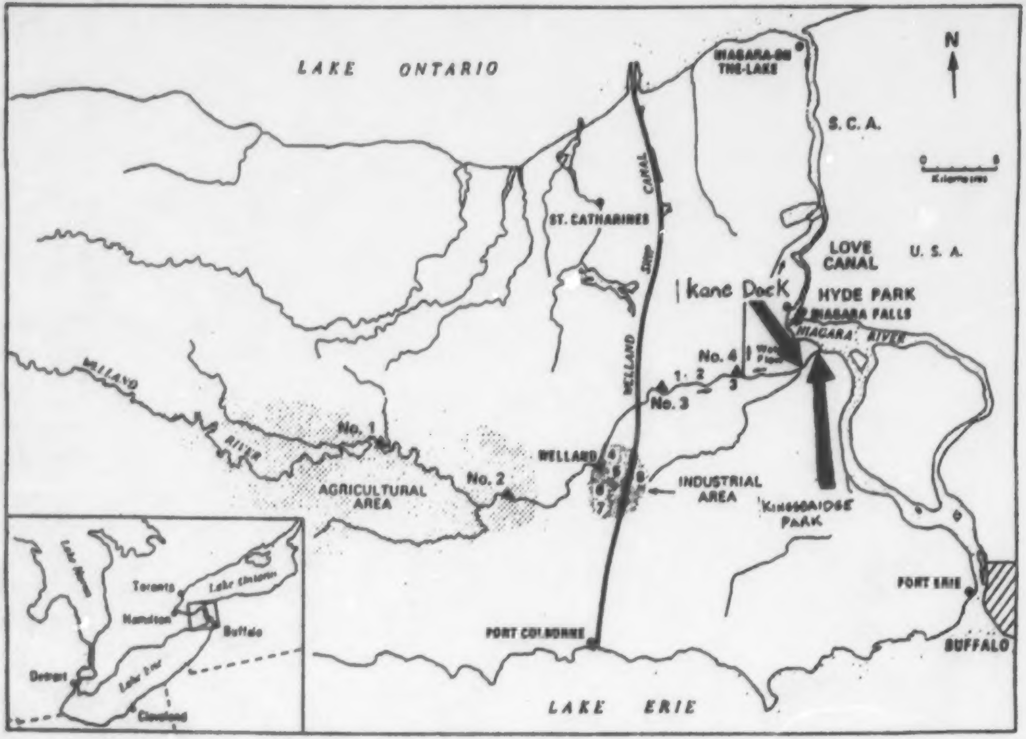
LAKE ONTARIO
NIAGARA-ON-THE-LAKE
N
S. C. A.
0 8
Kilometres
ST. CATHARINES
WELLAND SHIP CANAL
LOVE CANAL
U. S. A.
Kane Dock
HYDE PARK
NIAGARA FALLS
NIAGARA RIVER
No. 4
1 2 3
No. 3
WELLAND RIVER
No. 1
No. 2
WELLAND
4 5 6 7 8
INDUSTRIAL AREA
AGRICULTURAL AREA
KINGSBRIDGE PARK
FORT ERIE
BUFFALO
PORT COLBORNE
LAKE ERIE
Lake Huron
Toronto
Lake Ontario
Hamilton
Buffalo
Detroit
Lake Erie
Cleveland

Figure 1

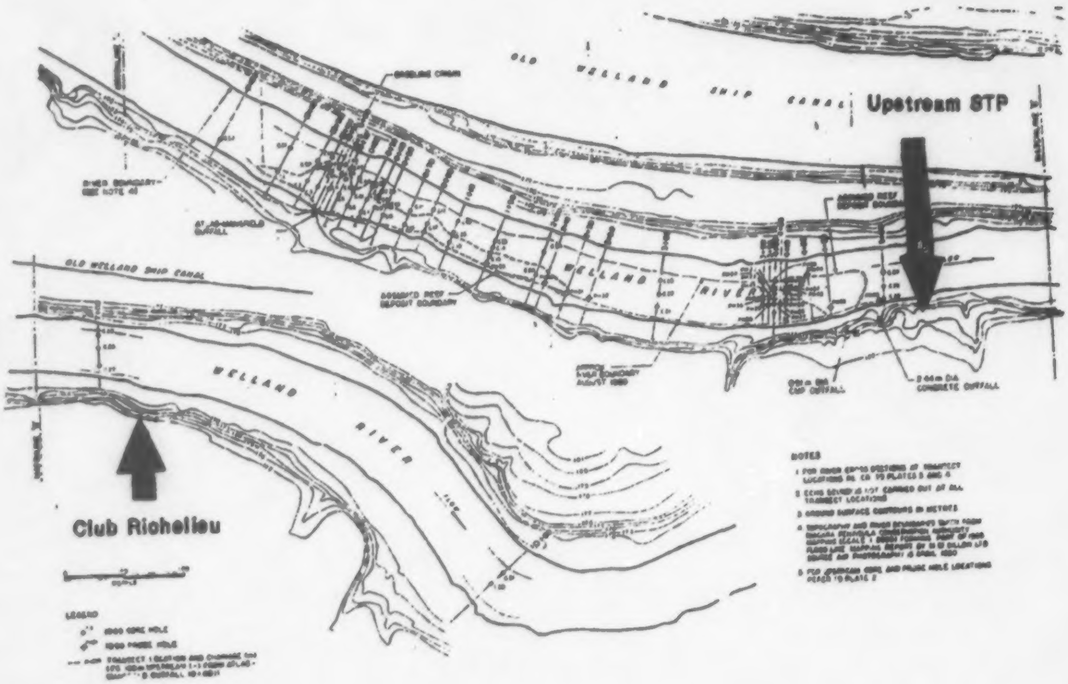
OLD WELLAND SHIP CANAL
Upstream STP
WELLAND RIVER
OLD WELLAND SHIP CANAL
WELLAND RIVER
Club Richelieu
NOTES
LEGEND

Figure 2

B15

MONITORING OF ORGANIC CONTAMINANTS IN AQUATIC FOOD-CHAINS

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Research at the Great Lakes Institute of the University of Windsor is directed to assist government and industry in the environmental management of contaminants. This includes providing tools and protocols for monitoring of contaminants in the Great Lakes. To accomplish these objectives a research program has been developed that consists of (i) Laboratory studies, focusing on specific mechanistic aspects of chemical dynamics, (ii) Field studies, testing and validating laboratory findings under field conditions, (iii) Computer modelling, which enables calculations involving the complexities encountered in the field, and which provides an up-to-date knowledge-base in an accessible and applicable form. To illustrate our research strategy, we present a summary of our studies of the chemical exposure dynamics in forage fish. The main objective of this presentation is to demonstrate how laboratory studies, field studies and food-chain/ecosystem modelling can be integrated to interpret biomonitoring data in terms of ambient contaminant levels in water and sediments of aquatic systems and in terms of chemical loads into the system.

PCB DYNAMICS OF POTTERSBURG CREEK, LONDON ONTARIO

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INTRODUCTION

In recent years, the mechanism for contamination in biota, especially top predators, has been greatly debated. Early food chain modelling embraced the concept of bioconcentration as being the mechanism responsible for the observed body burdens in aquatic organisms (Schneider 1982; Duursma et al. 1989). Bioconcentration states that the concentration in an aquatic organism can be attributed to the chemical concentration in the water, the octanol/water partition coefficient, and the lipid fraction of the organism. Considerable evidence has shown that this relationship does not always hold true for many organic chemicals including PCB's. Many experiments have shown that aquatic organisms are capable of bioaccumulating PCB's above concentrations which would be expected from water alone (Oliver and Niimi 1985; Gobas et al. 1987.). This would suggest that some other mechanism, such as biomagnification (ie. the uptake of a chemical through ingestion), is responsible for the contaminant levels in aquatic biota, especially those occupying the top of food chains (Thomann 1987; Shaw & Connel 1986).

The discovery of PCB contamination in Pottersburg Creek, London, Ontario, has provided an opportunity in gaining a better understanding of the movement of PCBs in aquatic ecosystems and the mechanism of PCB transfer to higher trophic levels. Moreover, the ultimate objective of this project is to develop a model in order to predict the time required for PCB levels in aquatic biota to reach the IJC (1975) aquatic life protection guideline of 100 ng/g.

MATERIALS AND METHODS

Collection and analyses of stream components, 1988 - 1989.

Samples of algae, aquatic macrophytes, various macroinvertebrates and fish were collected for biomass and PCB analysis at 4 sites along Pottersburg Creek (Fig.1). Water and sediment samples were collected by the Ministry of the Environment. Station 1 was the control site and Stations 2, 3 and 4 were located downstream of the point of contamination.

Invertebrates gathered for biomass and density determination were collected with a T-sampler enclosing an area of 0.052m^2, and sieved through a 300 μm bag. The samples were picked live in white enamel trays and subsequently preserved in 70% ethanol for later identification and enumeration. All organisms were identified to the lowest taxonomic level practical, usually genus,

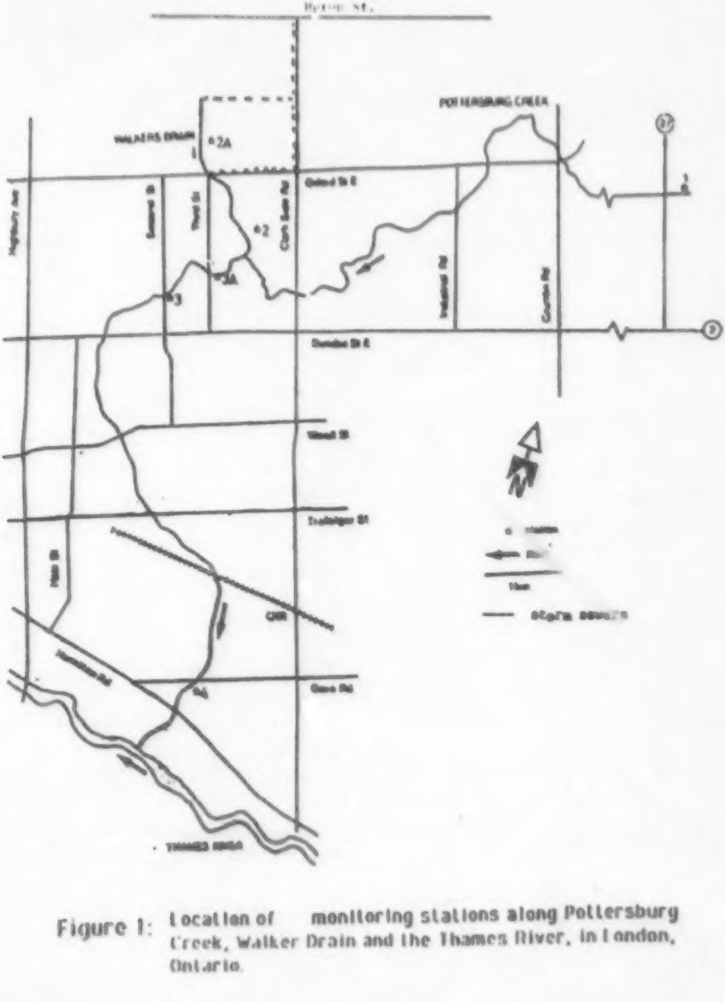
Byron St.
POTTERSBURG CREEK
WALKERS DRAIN
2A
2
3A
3
4
Oxford St E
Highbury Ave
Clarke Side Rd
Industrial Rd
Crumlin Rd
Dundas St E
Trafalgar St
CNR
Gore Rd
THAMES RIVER
1km
storm sewers

Figure 1: Location of monitoring stations along Pottersburg Creek, Walker Drain and the Thames River, in London, Ontario.

except for oligochaetes which were identified to species.

Invertebrates gathered for PCB analysis were collected with sieve buckets and picked live in white enamel trays until an adequate weight was obtained for analysis (ie. 3g or more). Animals were separated into their respective classes (eg. oligochaetes, chironomids, leeches) and weighed to the nearest 0.01g. Samples were subsequently wrapped in hexane-rinsed aluminum foil, placed in plastic Whirl-Pak bags and kept frozen until analysis. The samples were analyzed for total PCBs and results were reported on a wet-weight basis. Analyses were carried out at the Ontario Ministry of the Environment's laboratory in Rexdale using packed column gas chromatography.

Construction of a Food Web

Fish were collected with a seine net from Stations 1,2,3 and 4 and preserved in formalin. Collections were made in the summer and winter of 1988 and the summer of 1989. Fish stomachs were dissected and a list of food items was compiled. A food web of Pottersburg Creek was synthesized from feeding observations and gut contents analysis. Points of PCB entry and loss were also identified.

Determination of PCB uptake and depuration rates

Uptake experiments were set up for the following biota: crayfish, leeches, fish, and oligochaetes. Crayfish were captured in the fall of 1989 from the Eramosa River, Guelph, Ontario. A total of 32 crayfish were placed in wire cages measuring 15cm x 15cm x 15cm, with 4 crayfish per cage. Leeches (*Nephelopsis obscura*) were purchased from a local bait dealer. Approximately 15 leeches were placed in each of 5 triangular cages (30cm sides) made of wire and nylon screen which had a mesh size of 2mm. Creek chub (*Semotilus atromaculatus*) were collected from the control site, Station 1. Approximately 35 fish were placed in a single wire cage 80cm x 80cm x 15cm. Oligochaetes were purchased from a local pet store and approximately 15 grams of worms were placed in each of 5 metal tins (15cm height, 10 cm diameter) containing PCB contaminated sediments collected from Station 2. The sediments were sieved through a 300um screen to remove indigenous worms and large particulate matter. The tops and bottoms of each can were replaced with 300um mesh screening and secured with rubber bands.

The cages containing the biota were anchored to the stream bed with bricks at the contaminated site (Station 2) and subsequently collected after 4,6,10,18 and 34 days. Control groups were placed at the uncontaminated site, Station 1, and collected after 34 days. Each group of animals was weighed live to the nearest 0.01g, wrapped in hexane-rinsed aluminum foil, placed in Whirl-Pak plastic bags, and frozen until analysis. Three replicate samples were submitted for each time period. In addition, samples of all groups of animals were submitted for pre-exposure analysis .

The experimental design and protocol was the same for the depuration study with the exception that the animals were collected from the contaminated site (Station 2), and anchored to the stream bottom at the control site (Station 1).

RESULTS AND DISCUSSION

PCB residues in algae and aquatic macrophytes

In 1988, algae (*Cladophora sp.*) and aquatic macrophytes (*Potamogeton sp.*) collected at Station 2 were able to accumulate substantial quantities of PCBs, 150 ng/g and 770 ng/g, respectively. No PCBs were detected in algae and aquatic macrophytes at Station 3. Several authors have documented the uptake of chlorinated hydrocarbons by phytoplankton (Biggs et al. 1980; Sodergren and Gelin 1983) aquatic macrophytes (Strek and Weber 1982) and filamentous algae e.g. *Cladophora sp.*, (Mowrer et al. 1982; Larsson 1987). Phytoplankton and Cladophora are able to rapidly sorb PCBs from the water and the uptake initially follows first order kinetics (Larsson 1987). Thus, the partitioning process governs PCB uptake and in turn is dependent on the concentrations of PCBs in the water (Larsson 1987). In March 1988, PCB concentrations in water at Station 4 were 680 ng/g. PCBs bound to sediments may be redistributed to the water by bioturbation (the activity of benthic invertebrates in the sediment), and desorption (Klump et al. 1987; Karickhoff and Morris 1985) and thus made available to algae and phytoplankton.

As no metabolism or elimination of PCBs has been recorded in algae (Hutzinger et al. 1974), the rapid adsorption and uptake of PCBs by algae and aquatic macrophytes constitute an additional means for the introduction of these compounds into food webs (Mahanty 1986). Algae and aquatic macrophytes are consumed by scrapers, ie. snails and shredders,ie. crayfish. Algae are also consumed by a variety of fish in Pottersburg Creek. Analysis of gut contents has revealed that filamentous algae are the primary diet of the northern redbelly dace (*Chrosomus eos*) and the stoneroller (*Campostoma anomalum*). Common shiners (*Notropis cornutus*) and blacknose dace (*Rhinichthys atratulus*) also consume filamentous algae but to a lesser extent. Thus algae and aquatic macrophytes appear to be significant vectors in the transfer of PCBs to the higher trophic levels in Pottersburg Creek.

PCB residues in snails and crayfish

PCB residues in snails and crayfish can be attributed to the consumption of algae and aquatic macrophytes. In 1988, *Helisoma sp.* collected from Station 3 had a PCB residue of 360 ng/g and young of the year crayfish from Stations 2, 3 and 4 had residues of 960 ng/g, 720 ng/g and 320 ng/g, respectively. No PCBs were detected in Station 1 biota. Decreasing body burdens in crayfish indicate a reduction of PCB availability with increasing distance from Walkers Drain (Stn. 2). Older crayfish from Station 3 were noted to accumulate 40% more PCBs than young of the year. This would suggest that length of exposure, coupled with higher lipid levels in the older individuals, may have an effect on PCB bioaccumulation. In addition, crayfish eat detritus, and other organisms

(Hynes 1970), which in turn are known to accumulate or sorb PCBs. Thus, bioaccumulation may be further facilitated via this pathway and account for the higher body burdens observed in crayfish.

In 1989, snails collected at Station 3 showed no accumulation of PCBs, however, these may have recently drifted from upstream uncontaminated areas. Consequently residues may not reflect true availability. PCB residues in crayfish collected from Station 2, 3 and 4 varied depending on the size of the animal as well as the lipid content albeit, concentrations were noted to be lower than in the previous year. Crayfish and snails are eaten by a variety of fish (Scott & Crossman 1972). Gut contents analysis confirmed the ingestion of snails by creek chub (*Semotilus atromaculatus*) in Pottersburg Creek, however no crayfish were found in the stomachs of the fish. Therefore, snails serve as a vector for the distribution of PCBs to fish which occupy a higher trophic level.

PCB residues in oligochaetes and chironomids

PCB residues in oligochaetes and chironomids were among the highest for 1988 biota, reaching concentrations of 3030 ng/g and 1890 ng/g respectively in the summer months. Initial bioaccumulation by midges has been shown to be very rapid with steady state concentrations being reached in 4 to 5 days (Swindoll & Applehans 1987). In addition, benthic organisms, such as worms and chironomids, ingest sediment (Roberts and Meier 1982) and PCB contaminated organic particles after they settle on the sediment (Landrum & Scavia 1983; Oliver 1984). Meier and Rediske (1984) have been able to show that larvae of the midge *Glyptotendipes barbipes* can accumulate significant concentrations of PCBs from substrate feeding alone. Ingestion increases exposure surfaces as well as decreases distances for diffusion and thus facilitates uptake of sediment-sorbed compounds (Swindoll & Applehans 1987).

In 1989, PCB concentrations in worms and chironomids have decreased to 900ng/g and 200ng/g respectively perhaps reflecting a decrease in the availability of these lipophilic compounds to lower trophic level organisms.

PCBs have been shown to be poorly eliminated from benthic organisms (Swindoll & Applehans 1987; Meier & Rediske 1984). In Pottersburg Creek analysis of fish stomachs has shown that midge are consumed by almost all fish. In addition, several authors have shown that fish such as creek chub consume worms (Gilliam et al. 1989). Thus it is probable that chironomids and worms serve as major vectors for the contamination of the higher trophic levels ie. fish and leeches.

PCB residues in leeches

In the summer of 1988, PCB residues in leeches were 2000 ng/g at Station 2 and 1060 ng/g at Station 3. In 1989, residues dropped to 1100 ng/g at Station 2 and 700 ng/g at Station 3. The observed PCB concentrations in leeches can be attributed to the close proximity of the animals to the sediments but the main route is through ingestion of contaminated prey. Leeches (*Erpobdella punctata punctata*) captured from Pottersburg Creek were observed eating chironomids in captivity. As well, several authors have documented that the main food items of leeches are oligochaetes and chironomids (Davies et al 1981; Anholt 1986). The decrease of PCBs in leeches mirrors the decrease in their prey whereas sediment concentrations have fluctuated over the two year period.

Leeches are preyed upon by a variety of fish (Scott & Crossman 1973) but were only found in one fish from Pottersburg Creek. Therefore, it was concluded that leeches serve as intermediate vectors of PCBs transfer to fish in the creek.

PCB residues in fish

Eleven species of fish have been identified from Pottersburg Creek and can be grouped into four categories based on their primary diet: algae grazers; chironomid feeders; bottom ooze feeders; and general feeders.

Common shiners (*Notropis cornutus*) collected in July 1988 had lower PCB residues than johnny darters (*Etheostoma nigrum*) collected from the same stations. The observed differences can be attributed to the position of the fish in the water column as well as their diet. Johnny darters were found to feed primarily on chironomids which themselves exhibited very high PCB levels. On the other hand, analysis of common shiner fish stomachs revealed no preferred diet. However, it was noted that in the spring and early summer, their diet consisted primarily of surface insects. Gilbert (1964) found that common shiners usually feed off the surface but will take food off the bottom. In the fall and winter months, the common shiner switches its diet to detritus, sediment, silt or invertebrates depending on their respective availabilities. Thus, depending on the time of year, PCB residues in common shiners may vary depending on their diet.

PCB concentrations in common shiners and johnny darters varied in 1989 depending on station location and lipid content. Moreover, it was noted that PCB concentrations in both species of fish did not decrease over the two year period perhaps as a result of biomagnification as fish occupy the highest trophic level.

Food web of Pottersburg Creek

A synthesized food web of Pottersburg Creek is presented in Figure 2. Chironomids and worms are the major food items of almost all fish species except the northern redbelly dace and the stoneroller whose primary diet is filamentous algae.

Uptake and depuration rates

Preliminary uptake and depuration experiments (Table 1) have shown that invertebrates and fish are able to accumulate PCBs in a short period of time. Worms accumulated 400 ng/g PCB in 24 days while leeches accumulated a maximum of 160 ng/g in 18 days which then dropped to 120 ng/g after

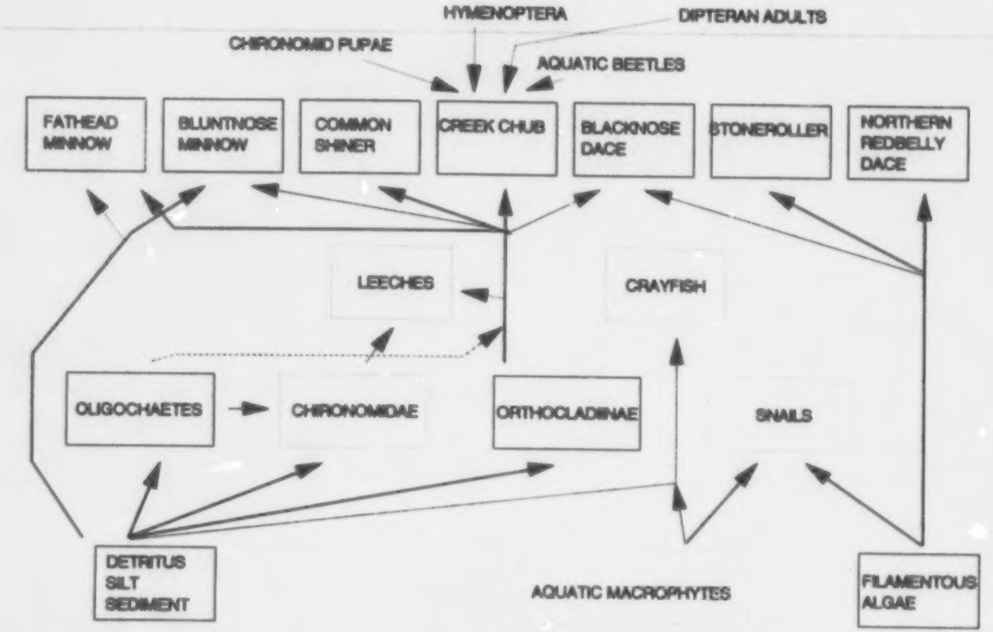
HYMENOPTERA
DIPTERAN ADULTS
CHIRONOMID PUPAE
AQUATIC BEETLES
FATHEAD MINNOW
BLUNTNOSE MINNOW
COMMON SHINER
CREEK CHUB
BLACKNOSE DACE
STONEROLLER
NORTHERN REDBELLY DACE
LEECHES
CRAYFISH
OLIGOCHAETES
CHIRONOMIDAE
ORTHOCLADIINAE
SNAILS
DETRITUS SILT SEDIMENT
AQUATIC MACROPHYTES
FILAMENTOUS ALGAE

FIGURE 2: FOOD WEB OF POTTERSBURG CREEK, STATION 2 ,SPRING-SUMMER.

28 days. However accumulations are not of the same magnitude as those of the resident biota collected in 1988 and 1989. Lower accumulations may be attributed to the short maximum time interval ie. 34 days, therefore, subsequent uptake and depuration experiments will be conducted for a longer period of time. In addition, the control experiments, which ran parallel to the uptake and depuration experiments, revealed that the cages were exerting a significant amount of stress on the animals resulting in weight loss and mortality. This was particularly evident in fish and crayfish who only accumulated approximately 40 ng/g PCB and 100 ng/g in 34 days. For these reasons, initial cages will be modified to minimize stress and allow foraging.

Modelling

Upon the completion of the uptake and depuration experiments, all available information and data collected from Pottersburg Creek will be integrated and placed into an ecological framework. PCB transfer rates between the different components of the stream (ie. fish, invertebrates, water, plants, etc.) will be deduced mathematically and subsequently incorporated into a simulation model in order to explore PCB dynamics in stream ecosystems. However, as all results are not yet available, modelling is still to be completed.

CONCLUSION

As reflected in the data, PCB concentrations in biota, water and sediments from Pottersburg Creek appear to be decreasing with time as well as along the length of the creek away from the point source. However, PCB residues in aquatic biota still remain above the IJC aquatic protection guideline of 100 ng/g indicating that a continuing source of PCBs remains within the creek or is entering the creek periodically.

From within the creek, the sediments are implicated as being a continuing source of PCBs to the biota. Scouring of bottom sediments caused by catastrophic drift, bioturbation and desorption processes continuously redistribute PCBs making them more available to aquatic biota. In addition, water and sediment samples collected from the storm sewer networks indicate that during times of heavy rainfall, there is a substantial influx of PCBs into the creek. The coupling of all these processes has attributed to the observed high PCB accumulations in biota. It is suggested that further biomonitoring of Pottersburg Creek continue until PCB levels in biota drop below 100 ng/g.

ACKNOWLEDGEMENTS

The authors are thankful to the Ontario Ministry of the Evnironment for financial assistance.

TABLE 2: PCB concentrations in caged biota from Pottersburg Creek, London, Ontario. Uptake and depuration experiments, 1989.

BIOTA	DATE	LOCATION OF CAGES(sta.)	DAY	SAMPLE WEIGHT (g)	% LIPIDS	PCB'S (ng/g)
CRAYFISH [Orconectes propinquus] uptake	89/10/03	-	Day 0 uptake	8.3	0.9	<20
				7.24	2.6	<20
				8.18	0.9	<20
	89/10/07	2	Day 4	4.57	2.9	70
				5.03	4.0	<20
				7.19	2.0	<20
	89/10/09	2	Day 6	7.35	1.9	<20
				8.05	1.5	<20
				6.77	?	?
	89/10/13	2	Day 10	6.42	2.6	<20
				6.08	2.2	<20
				5.26	2.4	<20
	89/10/21	2	Day 18	12.47	1.8	<20
				6.90	1.7	<20
				4.40	2.6	80
	89/11/06	2	Day 34	7.30	2.6	150
				7.07	1.7	70
				8.04	2.9	100
	89/11/06	1	Day 34 control	3.72	3.3	<20
				7.32	2.6	<20
LEECHES [Nephelopsis obscura] uptake	89/09/27	-	Day 0 uptake	4.40	2.3	<20
				3.72	2.9	<20
				3.11	3.1	<20
	89/09/27	2	Day 4	10.41	3.0	<20
				6.16	2.6	<20
				7.9	3.1	<20
	89/09/29	2	Day 6	8.73	2.7	60
				10.97	2.9	60
				8.00	2.0	50
	89/10/03	2	Day 10	3.63	3.6	60
				3.20	3.9	100
				3.01	3.6	100
	89/11/02	2	Day 18	4.00	2.2	160
	89/11/12	2	Day 28	3.06	2.7	120
	89/11/02	1	Day 40 control	3.71	3.9	<20
				4.15	4.6	<20
FISH [Semotilus atratulus] Uptake	89/10/09	-	Day 0	26.40	1.6	<20
				17.92	1.6	<20
				14.27	1.5	<20
	89/10/13	2	Day 4	21.86	2.0	<20
				16.61	1.0	<20
				16.60	2.0	<20
	89/10/15	2	Day 6	18.01	1.8	<20
				21.07	2.0	<20
				12.95	1.5	30

TABLE 1: [Cont..]

BIOTA	DATE	LOCATION OF CAGES(stn.)	DAY	SAMPLE WEIGHT (g)	% LIPIDS	PCB'S (ng/g)
	89/10/19	2	Day 10	21.42	1.8	30
				19.44	1.6	<20
				10.86	2.4	40
	89/10/27	2	Day 18	14.29	1.5	40
				17.27	1.5	<20
				23.19	1.6	<20
	89/11/12	2	Day 34	11.66	1.9	60
				10.33	2.3	40
				8.09	1.4	60
WORMS uptake	89/10/09	-	Day 0	5.18	7.7	<20
				5.00	7.8	<20
	89/10/13	2	Day 4	3.02	5.2	280
				3.02	5.9	200
	89/10/15	2	Day 6	3.92	4.3	320
	89/10/19		Day 10	5.44	5.7	300
	89/10/27	2	Day 18	2.25	4.3	270
	89/11/02	2	Day 24	2.19	5.4	400
FISH [Semotilus atrotulus] depuration	89/10/03	-	Day 0	26.62	2.5	650
				18.67	1.5	650
				18.81	1.8	320
	89/10/07	1	Day 4	26.57	13.9	1000
				22.21	3.0	720
				30.90	1.2	400
	89/10/09	1	Day 6	12.38	9.3	2000
				30.23	1.3	475
				14.97	5.0	600
	89/10/13	1	Day 10	14.27	1.4	450
				14.90	8.8	900
				7.74	3.2	730
	89/10/15	1	Day 0	16.83	2.2	600
			2nd set	14.07	1.3	1050
	89/11/02	1	Day 18	21.08	1.7	730
				12.05	10.3	700

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VOLUME I

SESSION B

WATER QUALITY RESEARCH

POSTER PRESENTATIONS

DEVELOPMENT OF AN IMPROVED SYSTEM FOR THE APPLICATION OF POWDERED ACTIVATED CARBON IN POTABLE WATER TREATMENT

by

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Powdered activated carbon (PAC), is widely used in Ontario and around the world for the removal of taste and odour from drinking water. More recently PAC has been finding use in the removal of toxic organics from drinking water either in the case of chronic low level contamination or occasional high levels resulting from an accidental spill. ZENON Environmental Inc. has undertaken a study for the Ontario Ministry of the Environment to develop an improved system for the application of PAC in water treatment plants and to develop a concept for a portable system suitable for response to specific short term treatment needs.

The Phase 1 study included the following:

1) Literature review
2) Identification of PAC systems
3) Development of process design criteria
4) Selection of two most promising PAC systems
5) Bench scale development and evaluation of two systems
6) Selection of one system for demonstration

Conventional PAC drinking water treatment for taste and odour control is by slurry addition prior to coagulation/sedimentation or granular filtration. The literature search did not reveal any alternative PAC contacting or separating systems being used or developed for drinking water treatment, however, a wide variety of systems for wastewater treatment are being used or developed. Two conventional PAC contacting and separation systems and ten alternative PAC systems were identified as potentially applicable for toxic contaminant removal from drinking water and suitable for initial evaluation.

The following criteria were established and used to evaluate the potential reactor alternatives.

a) Contact time greater than one minute.
b) Contact stratification.
c) Reliable separation.
d) Spill response.
e) Adaptable to existing facilities.
f) Process reliability.
g) Mechanical reliability.

Downflow PAC packed bed filtration and multistage crossflow filtration met all of the criteria and were selected for development at bench scale.

In bench scale testing performance of downflow PAC packed bed filtration was proven to be unreliable due to the development of channels through the bed.

Crossflow ultrafiltration (UF) was proven to effectively separate PAC from an aqueous stream. The UF fluxes observed were relatively high and stable. A multistage UF system is necessary to achieve contact stratification but is technically feasible for the removal of toxic organics from drinking water.

In the second phase of work a pilot scale Powdered Activated Carbon/Cross Flow Filtration PAC/CFF system was constructed and operated at the Brantford Water Treatment plant.

The performance of the system was evaluated at different operating conditions and with odour and other organic chemicals spiked into the feed. The CFF flux was consistent and stable during the tests averaging 114 L/m^2/hr. The process consistently removed turbidity to less than 0.03 NTU and total coliforms to less than 2 counts/100 ml. The removal of dissolved organic carbon (DOC) and total trihalomethane forming precursors (TTHMFP) was marginal at PAC dosages of 5-10 mg/L but significant (25% and 35% removal) at higher dosages of 56 mg/L.

The capital and operating costs for 1 MGD and 0.1 MGD PAC/CFF systems were estimated. The total costs for the 1 MGD PAC/CFF treatment ($2.38/1,000 gal) are higher than for conventional coagulation/filtration treatment followed by GAC ($1.52/1,000 gal). The total cost for the 0.1 MGD PAC/CFF treatment process at a high PAC dosage of 1,000 mg/L is $6.22/1,000 gal.

The treatment costs for the PAC/CFF are high but the process has the following advantages:

1) Provide guaranteed removal of turbidity and bacteria.
2) Easy startup and suitable for operation with minimal attendance.
3) Requires no guesswork or chemicals to obtained required treatment.

In view of these advantages the system is a viable response to emergency situations but may not be suitable as a replacement for conventional treatment followed by GAC unless the feed water is highly variable in turbidity or colour. With time, as membrane costs become lower however, the cost as well as water quality advantage are likely to favour this option for permanent systems.

BP2

Geochemical Associations of Cd, Cu, Pb and Zn with Suspended Particulates in the Don River. Lesley A. Warren* and Ann P. Zimmerman. Department of Zoology, University of Toronto, Toronto, Ontario, Canada.

The Don River drains a highly urbanized watershed of 376 km^2 and runs approximately 30 km through Metropolitan Toronto before discharging into Lake Ontario through the Keating Channel. There are over 1400 street run-off and industrial discharge outfalls on the river as well as a major sewage treatment plant and a snowmelt yard. Increasing problems with contaminated sediments in the Keating Channel and the Harbour have led to questions about sources of sediments and associated metal loads, development of in-place pollutants, relationships between sediment composition and water quality and whether in-place pollution and its effects on aquatic ecosystems can be predicted.

The purpose of the present study was to investigate the geochemical associations of 4 trace metals, Cd, Cu, Pb and Zn, within the pool of total SPM *in situ* in the Don River, located in Metropolitan Toronto; and to determine the relative importance of various trace metal pools in the SPM fraction as trace metal carriers within this system. This work represents the first phase of a larger ongoing study on the Don to determine the role of SPM as a transport vector of trace metals, and whether predictive relationships among specific discharge sources of metals and/or solids to the Don, and the geochemical associations of trace metals with SPM *in situ* can be derived.

A total of 37 suspended sediment samples were collected at 4 sites on the Don River over a 12 month period. These samples were analysed for the trace metals Cd, Cu, Zn and Pb in 4 operationally defined geochemical phases:(1) Leachable ("exchangeable and carbonate associated"); (2) Reducible ("oxides"); (3) Oxidizable ("organics"); and (4) Residual ("mineral phases"). While concentrations of suspended sediment and total metal were highly variable in time and space, in general there was an increase in both in a downstream direction, thus, increasing metal loads in this direction. Metal speciation patterns were relatively constant despite variability in absolute concentrations. With the exception of Cd, very small proportions of metal were found associated with the exchangeable fraction. Cu was the only metal found in high proportions associated with the organics fraction. The two major sediment carrier phases in the Don River are the oxides and residual minerals. As these phases form stable complexes with trace metals, the fate of trace metals in this system is intimately tied to the suspended particulate fraction. PCA analyses showed that a major proportion of the variance in metal concentrations is explained by geochemical phase.

BP3

THE EFFECTS OF AGRICULTURAL DRAINAGE ON SEDIMENT AND WATER QUALITY LOADINGS.

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INTRODUCTION

The principal objective of this project was to gain an understanding of the pathways and fates of agricultural chemicals (fertilizers and pesticides) applied to tile-drained fields. Removal of valuable pesticides, fertilizers and topsoil by surface or subsurface drainage represents an economic loss to agriculture and a potential pollution hazard to receiving waters. In order to evaluate this potential impairment of water quality, there is a need for accurate prediction of chemical contaminant and sediment loadings for different environments, loading conditions, and agricultural management strategies. This then is an area of interest to both the agricultural community and Environment Ontario. The specific objectives of the work were (i) to develop a continuous, physically-based hydrologic simulation model to represent processes for contaminant transport on the surface, through the soil profile and into the tile drains; (ii) to undertake field studies to define the model's physically-based parameters such as saturated hydraulic conductivity, soil type and depth, drainable porosity, infiltration characteristics, chemical transport and decay coefficients; (iii) to test agricultural management practices in conjunction with prevailing climate as they may influence nutrient or pesticide loss from the fields through the tile drains.

MODELLING TRANSPORT AND FATE OF PESTICIDES UNDER TILE DRAINAGE

A previous research project funded by Ontario Environment involved the development of TILE, a continuous, physically-based hydrologic (water quantity) simulation model for tile-drained agricultural fields and basins. The challenge in development of water quality algorithms for use with the existing model was to incorporate significant processes within the existing framework in order to model chemical constituent storage, transport and transformation.

The conceptual representation of constituent migration within the framework provided by the TILE hydrologic model is illustrated in Figures 1 and 2. The control volume modelled is a single tile-drained agricultural field. Water is input as rainfall and exits by way of evapotranspiration, tile flow or surface runoff.

Constituent mass is input by human application and is allowed to leave through tile flow, surface runoff and a loss function which replicates the effects of a number of chemical and physical loss processes.

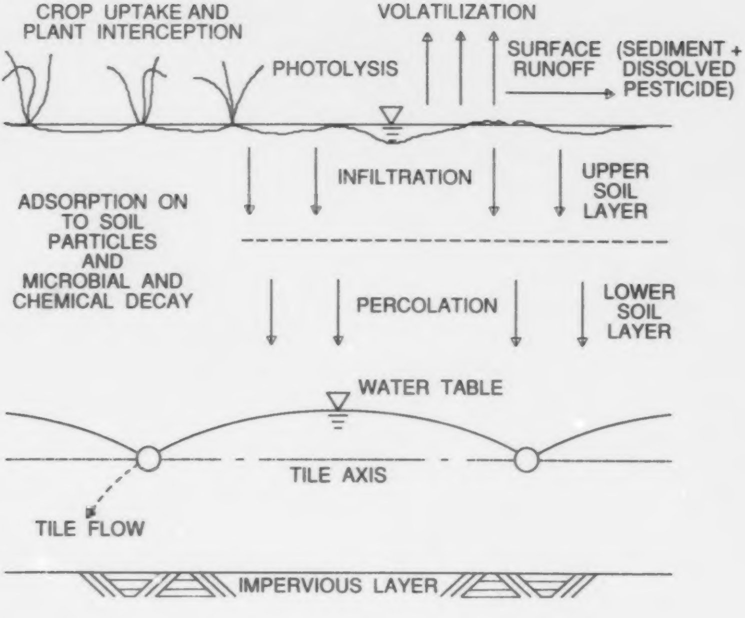
CROP UPTAKE AND PLANT INTERCEPTION
VOLATILIZATION
PHOTOLYSIS
SURFACE RUNOFF
(SEDIMENT + DISSOLVED PESTICIDE)
INFILTRATION
UPPER SOIL LAYER
ADSORPTION ON TO SOIL PARTICLES AND MICROBIAL AND CHEMICAL DECAY
PERCOLATION
LOWER SOIL LAYER
WATER TABLE
TILE AXIS
TILE FLOW
IMPERVIOUS LAYER

Figure 1. Field level processes - system modelled

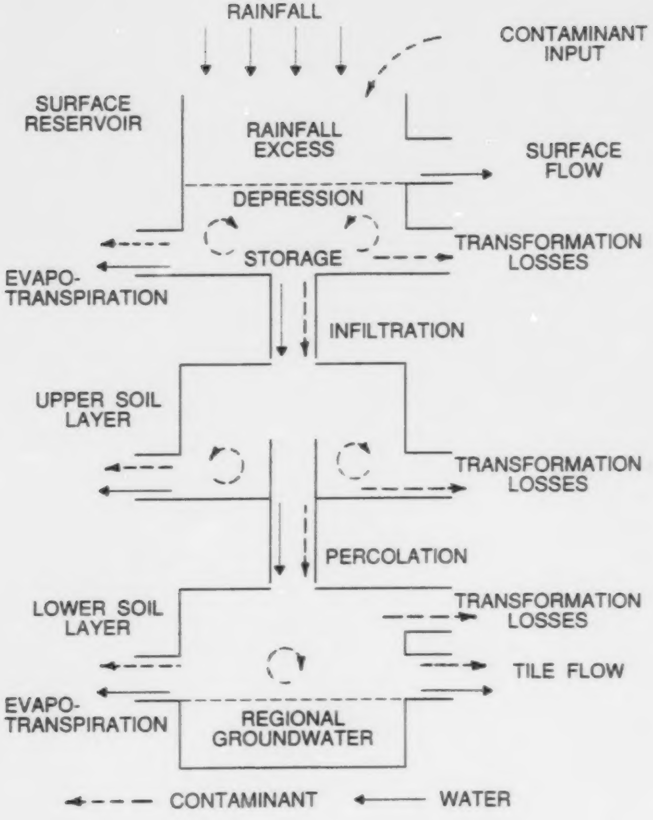
RAINFALL
CONTAMINANT INPUT
SURFACE RESERVOIR
RAINFALL EXCESS
SURFACE FLOW
DEPRESSION
STORAGE
TRANSFORMATION LOSSES
EVAPO-TRANSPIRATION
INFILTRATION
UPPER SOIL LAYER
TRANSFORMATION LOSSES
PERCOLATION
LOWER SOIL LAYER
TRANSFORMATION LOSSES
TILE FLOW
EVAPO-TRANSPIRATION
REGIONAL GROUNDWATER
CONTAMINANT
WATER

Figure 2. Conceptual representation - water quality model

Constituent mass storage is modelled by three storage reservoirs:

i) a surface storage reservoir which allows for the constituent to leave the system through the control volume boundary carried by generated surface runoff or to enter the soil storage reservoirs along with infiltration water,

ii) an upper soil layer storage reservoir from which the constituent mass may enter the lower soil storage reservoir through percolation, and

iii) a lower soil layer storage reservoir from which the constituent mass may be discharged and lost to the system through tile drainage.

Constituent mass transmission pathways are:

i) application of the constituent mass to the field by human action,

ii) routing of constituent mass to the edge of the field by surface flow and subsequent loss of the mass through the control volume boundary,

iii) migration of constituent mass from the surface mass storage reservoir to the upper soil layer along with infiltration water,

iv) migration of constituent mass from the upper soil layer storage reservoir to the lower layer along with percolation water, and

v) routing of constituent mass to the tile drains and subsequent loss to the control volume through tile flow.

The TILE quality model allows for application of a loss function conceptualized to represent a number of physical, chemical and biological processes acting within the agricultural field system to reduce the constituent mass available for transport to all three of the mass storage reservoirs. The most significant processes lumped within the representative loss function are dispersive or turbulent flow distortions to advective constituent transport, constituent adsorption onto soil particles, and physical (photolysis, volatilization), chemical (hydrolysis and other chemical reactions) and biological (microbial decay and plant interception) transformation processes.

Methodologies by which agricultural chemicals are applied to farm fields can be divided into two categories: i) surface application by which the chemical is placed onto the soil surface as a liquid spray or solid broadcast, and ii) subsurface application where the chemical is incorporated directly into the upper layer of the soil. Subsurface application is becoming more popular since it is believed to reduce post-application losses due to wind action, surface runoff and transformation processes such as volatilization and photolysis. The model allows for specification of the application method by the user in conjunction with specification of the time of application. If a surface application method is indicated, the program responds by assigning the input mass to the surface storage reservoir. If, however, an incorporation method is specified, the input mass is assigned directly to the upper soil storage reservoir.

Pesticides commonly applied to farm fields are often formulated as powders or liquids with low solubilities in water. To provide an accurate model of the behaviour of such undissolved chemical species, two procedures were incorporated into the TILE quality model. The first procedure allows the user to input a laboratory or field-corrected solubility in water for the chemical constituent of interest. The model responds to the input solubility value by limiting the amount of chemical permitted to dissolve in the water available in a specific reservoir to the level provided for by the chemical solubility. In addition to the chemical solubility in water, review of the physical system of an agricultural field indicates that there will be a limiting quantity of water below which it is unlikely that a chemical could be dissolved and mixed uniformly within a particular storage reservoir. The TILE quality model allows for consideration of this 'mobility threshold' for each of the chemical application methodologies. If surface application is specified, then the mobility threshold corresponds to a minimum depth of water present in depression storage as a result of water inputs to the system. Thus it is possible for a small amount of rain to fall upon the field and infiltrate into the upper soil storage reservoir without causing any chemical mass to move with it. If, however, an incorporation method is chosen, then the mobility threshold necessitates that the specified volume of water above the field capacity be present within the upper layer soil storage reservoir for solution, mixing and transfer of the chemical constituent to occur.

MODEL TEST RESULTS

The use of the model for both real and synthetic rainfall events demonstrated the relative importance of i) pesticide application methods, ii) rainfall occurrences following application, and iii) soil characteristics on the transport of contaminants to the tile drains and thence to receiving waters. The poster display illustrates water quantity and quality hydrographs for differing situations noted above. Of particular interest is the half life of the pesticide in the upper layer (where it is available for crop uptake) for the various rainfall sequences and application methods modelled.

BP4

CHRONIC EFFECTS OF THIOCYANATE ON FRESHWATER FISH: DEVELOPMENT OF A WATER QUALITY CRITERION

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Thiocyanate (SCN^-) is an inorganic anion that has specific antithyroidal properties as an inhibitor of iodide (I^-) uptake and organification (Wolff, 1964; Yamada et al., 1974; Green, 1986). The antithyroidal properties of SCN^- have been recognized in mammals for some time, but investigations regarding antithyroidal effects in aquatic organisms have been limited to endocrinological studies in which SCN^- was administered by intraperitoneal (ip) injection (Singh, 1969; Singh et al., 1977; Eales and Shostak, 1983).

Thiocyanate has also been found to inhibit halide transport across biological membranes such as gills (De Renzis, 1975; Epstein et al., 1975; Maetz, 1976), and possibly the intestine (Katz et al., 1982), as well as reduce phosphorous (P) and I^- uptake by ovaries (Lindsay et al., 1966; Singh et al., 1977).

Cyanide (CN^-) is used by the mining industry in the extraction and concentration of gold from gold ores. As a result, cyanides are routinely present in mine effluents in considerable quantities. This situation has long been recognized as an environmental problem and has resulted in the establishment of an Ontario water quality objective for CN^- (0.005 mg/L, as HCN) (Ontario Ministry of the Environment, 1984).

The detoxification and recovery of CN^- from gold mill effluents often results in the presence of significant amounts of SCN^- in mill effluents. Thiocyanate levels of up to 168-680 mg/L have been detected in effluents following SO_2-air treatment (Huaitt et al., 1983). Metabolic SCN^- may be formed by aquatic organisms during the detoxification of CN^- present in industrial effluents or from the metabolism of naturally occurring dietary CN^- precursors, such as cyanogenic glycosides and nitriles.

Based upon lethality data (Doudoroff, 1976; Heming et al., 1985; Speyer and Raymond, 1988), SCN^- appears to be much less toxic than CN^-. Information on the chronic toxicity of SCN^- in fish is absent, although implications have been made (Leduc,

1984) that the chronic effects of CN^- exposure may actually be due to SCN^-. Due to the lack of sufficient information on the chronic toxicity of SCN^-, there is currently no water quality objective for SCN^- in Ontario.

The objective of our research was to obtain sufficient data on the chronic toxicity of SCN^- on survival, growth, metabolism, and reproduction of freshwater fish to permit the development of a water quality criterion.

The study has been divided into four phases:

1) A 16 week exposure of rainbow trout fry to SCN^- to determine effects on survival, growth, and physiology,

2) A life-cycle study to determine the impact of sublethal SCN^- exposure on the reproductive capacity of fathead minnows,

3) A 16 week exposure of rainbow trout fry to SCN^- or CN^- to determine the contribution of CN^- to sublethal SCN^- toxicity, and

4) A preliminary field study to determine if SCN^- is present in waters receiving effluent from gold mines and if physiological changes detected in laboratory fish in response to sublethal SCN^- exposure were present in feral fish.

METHODS AND RESULTS

Chronic rainbow trout exposure studies

Triplicate groups of juvenile rainbow trout (3 g) were continuously exposed to nominal SCN^- concentrations of 40, 80, 120 and 160 mg/L for 16 weeks. Trout were pair-fed a practical trout diet (GRT-70) (Cho et al., 1974) and weighed every two weeks to determine growth rates and provide a routine stressor to measure the expression of Sudden Death Syndrome (SDS) within each treatment population. Feed intake and mortalities were monitored daily.

At the end of the 16 week growth study, fish were anaesthetized in MS222, killed by cervical dislocation, and length, weight, splenosomatic and hepatosomatic indices, hematocrit, and hemoglobin were measured. Plasma samples for the colourimetric determination of total cyanide-reactive substances (Lambert et al., 1975) and thyroxine (T_4) were obtained by caudal peduncle severance. For thyroid histology, the entire lower jaw was removed from treated and pair-fed control fish, fixed in 10% buffered formalin, sectioned longitudinally, and stained with hematoxylin and eosin for routine histological observation.

Data were examined for normality and homogeneity of variance by the examination of residuals. One-way ANOVA, using $\log_{10}$ transformed data, was used to determine separately the effects of treatment levels and control food consumption levels on the response variables. Two-way ANOVA was then used to detect differences between treatments and their matched controls.

Mortalities and physical observations

Mortalities increased with SCN^- concentration, with all fish exposed to 160 mg/L dying by 12 weeks, and approximately 40% of the fish exposed to 120 mg/L dying by the end of the growth trial. SDS was apparent at the two highest concentrations of SCN^-, with varying proportions of the population at each treatment expressing SDS after weighing. Mortalities in the 40 and 80 mg SCN^-/L groups were minimal.

Cranial deformities were expressed to a varying degree in all SCN^--exposed trout, the severity of deformity increasing with SCN^- concentration. This condition was characterized by the small size of the head of the trout in relation to the body. Operculae were often shortened or crumpled, exposing gill filaments. Pigmentation changes were apparent as the transitory darkening of individual fish within tanks receiving thiocyanate.

Physiological parameters

Hepatosomatic (HSI) and splenosomatic (SSI) indices were significantly lower in exposed fish (HSI, $P=0.0001$; SSI, $P=0.0006$) relative to controls. HSIs decreased with increasing SCN^- concentrations ($P=0.0334$), but no dose response was apparent for SSIs ($P=0.3311$). Condition factor was not different between controls and treatment means ($P=0.3107$) and was not affected by SCN^- level ($P=0.5303$).

Fish exposed to SCN^- developed an anemia characterized by decreases in hemoglobin (Hb) and hematocrit (Ht). Hb and Ht treatment means were significantly lower (Hb, Ht, $P=0.0002$) relative to controls. Ht levels showed trends towards decreasing (Ht, P=0.1078) with increased SCN^- concentrations, while Hb levels did not show a dose response (P=0.5669). Plasma total cyanide-reactive substances increased (P=0.0106) with waterborne SCN^-, while plasma T_4 levels were lower (P=0.0284) in treated fish compared to controls and no dose response was apparent (P=0.67), due to the high variability between tanks within treatments (P=0.0421).

Histology

Histological changes were most prominent in the thyroid, with hypertrophy and hyperplasia of the thyroid follicular epithelium in all fish exposed to SCN^-. The number of follicles present in treated fish increased when compared to controls. The changes affecting the thyroid can be best characterized as "diffuse hyperplastic goitre". Control fish had low numbers of large follicles, most filled with eosinophilic colloid, and lined by a low cuboidal or squamous epithelium.

Fathead minnow reproduction study

Juvenile fathead minnows (≈4 months old) were continuously exposed to SCN^- concentrations of 0.05, 1.1, 7.3, 16.6, or 32.6 mg/L for 124 d. Since no secondary sexual characteristics were evident at the beginning of the exposure period, ten fish were later thinned out to 2 males/4 females per tank. After 3 weeks of exposure, spawning substrates were introduced into the test system. Development of secondary sexual characteristics and spawning behaviour were monitored. Reproductive parameters (time to first egg production, number of eggs produced, hatchability) and larval survival and incidence of deformities were monitored. After 124 d, fish were anaesthetized in MS222, and length, weight, and hematocrit were measured. Blood samples were taken by caudal peduncle severance for plasma SCN^- determination by HPLC. Fish were then fixed whole in 10% buffered formalin for routine histological observation.

The NOEC for reproductive performance was between 1.1 and 7.3 mg/L in the water and at about 2.5 mg SCN^-/L in the plasma. Exposure to waterborne SCN^- levels of ≥7.3 mg/L resulted in the development of overt goitre, incomplete sexual maturation, decreased egg production, and increased mortality and time to first spawn.

Embryonic development and larval mortality to 3 d post-hatch were monitored in eggs spawned by adults exposed 0.05 and 1.1 mg SCN^-/L and subsequently exposed to 0.05, 1.1, 7.3, 16.6, and 32.6 mg/L. Treatment effects were determined by split plot ANOVA. Adult thiocyanate pre-exposure level increased percent eyeup, hatch, and eyed eggs to hatch, while decreasing larval mortality and time to hatch. Egg incubation SCN^- concentration had no significant effect on these parameters.

Eggs spawned by adults exposed to 0.05, 1.1, and 7.3 mg/L were reared to adult stages while monitoring reproductive response. Only fish exposed to 0.05 or 1.1 mg SCN^-/L spawned successfully, while fish exposed to 7.3 mg/L matured, but developed overt goitre and did not spawn. Control larvae placed in 16.6 or 32.6 mg SCN^-/L developed overt goitre, exhibited poor growth with complete mortality by 8 weeks.

After the 124 d exposure period, adults exposed to 0.05, 1.1, 7.3, or 16.6 mg SCN^-/L were transferred to SCN^--free water for 30 d and reproductive response was monitored. Eggs were produced by all groups of fish. Time to first spawn increased with SCN^- pre-exposure concentration, with a marginally significant increase in larval deformities in the 16.6 mg/L group.

Rainbow trout SCN^-/CN^- exposure study

Duplicate tanks of juvenile rainbow trout were exposed for 16 weeks to either 40 mg SCN^-/L, 5 mg SCN^-/L, 15 ug CN^-/L, 5 ug CN^-/L, or no toxicant. At the end of 16 weeks, fish were killed by an overdose of anaesthetic (MS222) and weighed. Blood was collected by caudal peduncle severance for hematocrit determination and plasma samples. Plasma SCN^- was determined by HPLC (Brown et al., in preparation) and plasma thyroid hormones by radioimmunoassay. The peritoneal cavity was opened, spleen and liver removed, weighed, and HSIs and SSIs calculated. Thyroid, liver, spleen, kidney and gonad were prepared for routine histological observation as described previously.

Standard ANOVA procedures were used to detect main effects of toxicant exposure. Normality and homogeneity of variance of the data was determined by examination of residuals, and ANOVA was performed on $\log_{10}$ transformed data if these assumptions were violated. *A posteriori* comparison of means was conducted Tukey's HSD (α=0.005).

Exposure to 40 mg SCN⁻/L for 16 weeks decreased final body weight, HSI, SSI, and hematocrit compared to all other treatment groups. Plasma T_3 levels were marginally depressed in fish exposed to 40 mg SCN⁻/L, but plasma T_4 levels did not appear to be affected, possibly due to the within tank variability. T_3/T_4 ratios were not affected by any treatment. Plasma SCN⁻ levels of treated were elevated above control levels, where no SCN⁻ was detected in plasma. Fish exposed to 40 and 5 mg SCN⁻/L had mean plasma SCN⁻ levels of 63.7 and 10.1 mg/L, respectively. Groups exposed to CN⁻ (15 and 5 ug/L) had lower mean plasma SCN⁻ levels of 2.21 and 1.14 mg/L, respectively. Histological observations on selected tissues is currently underway.

Preliminary field assessment

Two gold mining regions of northern Ontario were selected as sites for the preliminary environmental health assessment of the impacts of SCN⁻-bearing effluents on aquatic systems. The two mine sites selected were the Hemlo area, east of Thunder Bay on the north shore of Lake Superior, and Larder Lake, located near Kirkland Lake.

No SCN⁻ was detected in any of the water samples taken from lakes in the Hemlo sampling area. Although some low level peaks appeared in a few plasma chromatograms, no definitive peaks of SCN⁻ were found in the plasma of suckers sampled from the Hemlo area. Any indications of plasma SCN⁻ levels are likely associated with the metabolism of cyanogenic components of the diet, and not related to any waterborne forms of SCN⁻ or CN⁻. These levels of plasma SCN⁻ are much lower than those found to be associated with goitre development in rainbow trout and would not be expected to result in any interferences with normal physiological processes.

Preliminary assessment of fish population data obtained from Herrick Lake, a lake downstream from the outfall area of the Hemlo mines, showed no apparent adverse effects on white sucker populations. Fish sampled in early September exhibited no gross lesions, had normal gonad development, and many year classes (including juveniles) were present in the sample.

Waterborne SCN⁻ (1.6 mg/L) was detected near the effluent outfall area of the Kerr-Addison mine in Larder Lake during the spring of 1989, but samples taken in July of the same year did not indicate the presence of SCN⁻. Thiocyanate was not detected in water samples from a spawning inflow of Larder Lake (Bear Creek), nor in any water samples taken from the control site, Raven Lake. Plasma samples of suckers taken from both Larder and Raven Lakes did not reveal the presence of any significant amounts of SCN^-.

Preliminary observations of thyroid tissues sampled from suckers indicates no apparent differences in thyroid tissue structure between fish sampled from test or control lakes in the Hemlo mining area. Fish sampled from Larder Lake appear to have fewer thyroid follicles than fish sampled from the control lake, Raven Lake, in the Kirkland Lake area. However, thyroid tissues from Raven Lake appear very similar in structure to those taken from fish in the Hemlo area.

DISCUSSION

The major consequences of the chronic sublethal exposure of rainbow trout to SCN^- are changes in thyroidal morphology characterized by a diffuse, hyperplastic goitre, alterations in plasma thyroid hormone, deformities in the cranial cartilage, and an anemia characterized by reduced hemoglobin, hematocrit, and splenosomatic indices. Chronic exposure to 5 mg SCN^-/L, 5 ug CN^-/L, or 15 ug CN^-/L elevated plasma SCN^- levels above control values, but did not result in the development of any of the signs characteristic of chronic SCN^- toxicity in rainbow trout.

Chronic exposure to SCN^- resulted in the development of overt goitre and reduced the expression of secondary sexual characteristics, spawning behaviour, and egg production in fathead minnows. The no observed effect concentration (NOEC) for egg production and spawning behaviour was between waterborne SCN^- levels of 1.1 and 7.3 mg/L. In terms of an internal body residue, depressed reproduction occurred in fathead minnows at plasma SCN^- levels of about 2.5 mg/L.

Sublethal SCN^- toxicity in rainbow trout and fathead minnows appears to involve thyroid function, as seen by histological evidence regarding goitre development, alterations in plasma thyroid hormone levels in trout, deformities in cranial cartilage development, and suppression of secondary sexual characteristics and egg production in mature fathead minnows. The dramatic reduction in egg production observed in fathead minnows at waterborne SCN^- concentrations between 1.1 and 7.3 mg/L appears to be the most sensitive indicator of SCN^- toxicity. Fertilization rates and larval growth and survival were less sensitive indicators, with a NOEC between 7.3 and 16.6 mg SCN^-/L. The development of overt goitre in fathead minnows at 7.3 mg SCN^-/L, but not in rainbow trout exposed to levels as high as 120 mg SCN^-/L may indicate differences in the metabolism of SCN^- between species.

Exposure of rainbow trout to sublethal levels of CN^- resulted in increased plasma SCN^- levels, but not to a level that resulted in an expression of the signs of chronic SCN^- toxicity.

Based upon the response of fathead minnow and rainbow trout to chronic SCN^- exposure, a water quality criterion of not greater than 1.1 mg SCN^-/L, the NOEC for reproduction in the fathead minnow, is suggested.

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BP5

ZOOPLANKTON COMMUNITIES AND WATER CHEMISTRY OF SUDBURY AREA LAKES: CHANGES RELATED TO pH RECOVERY.

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Lake acidification related to smelter emissions has been recognized in the Sudbury area since the study of Gorham and Gordon (1960). Studies conducted in Sudbury area lakes in the early 1970's (Sprules 1975, Roff and Kwiatkowski 1977, Keller 1981) showed pH to be a major determinant of zooplankton community structure, so that acidified lakes contained a community of fewer species than lakes of circumneutral pH. Above pH 5.0, zooplankton communities contained 9 to 16 species, with 3 or 4 dominant species. Below pH 5.0, only 1 to 7 species were present, with only 1 or 2 dominant species (Sprules 1975). Compared to unacidified lakes in northwestern Ontario, Sudbury area lakes contained very simple zooplankton associations in the 1970's.

Acidic atmospheric emissions in the Sudbury area have declined in recent years. Sulfur dioxide emissions from local smelters averaged 2.2 million tonnes/year between 1950 and 1972, 1.41 million tonnes/year between 1973-1977, and 0.68 million tonnes/year in 1979-1985 (Dillon et al 1986). In response to this reduction in acidic emissions, recovery from pH stress has begun in Sudbury area lakes. The term "recovery" is used here in the sense of a significant increase in pH and/or a decrease in metal concentrations, and does not necessarily imply a return to the pre-acidified state.

A 1981 survey of 249 northeastern Ontario lakes found that many Sudbury area lakes were still acidified, and that community structure of these lakes resembled that described for acidified lakes in the surveys of the 1970's (Keller and Pitblado 1984). The objectives of our study are to determine whether zooplankton community structure in Sudbury area lakes has changed relative to previous surveys, and if so, to investigate rates of plankton recolonization and direction of community change. We resampled 47 lakes in the La Cloche Mountain region southwest of Sudbury, which had been previously sampled by Sprules (1975). These data will be combined with data from 45 other Sudbury area lakes sampled by W. Keller (Ont. Min. of Envt., Sudbury office) in 1974-1976, 1981-1983 and 1988.

Zooplankton and water chemistry samples were collected from 47 lakes in the La Cloche Mountain region in August 1990. Preliminary results indicate that pH has increased by up to 1.6 pH units relative to 1971-1973 values. Zooplankton results will be presented at the conference. Zooplankton will be judged to be recovering if recolonization by species not present in earlier samples has occurred, decreased dominance by acid-tolerant species is observed and/or if community composition of previously acidified lakes has shifted to resemble that of circumneutral lakes.

BP6

THE RELATIVE EFFECT OF INDIVIDUAL ENVIRONMENTAL FACTORS ON INDICATOR BACTERIAL SURVIVAL;

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INTRODUCTION

Indicator bacterial survival in the water column and bed sediments of 3 rural streams was investigated by the Lake Simcoe Region and Metropolitan Toronto and Region Conservation Authorities between 1987 to 1989 (Harris and Walters, 1989). Bacterial die-off rates in water and sediment were shown to vary between streams, and within a single stream course, due to variations in chemical and physical characteristics. Seasonal variations in water temperature were shown to have an effect on survival. The rate of bacterial die-off moderately increased during summer months and declined in winter. In contrast, nutrient levels appeared to enhance bacterial survival, however the relationship was not well correlated.

Similar influence of these factors on bacterial longevity has been observed in other insitu studies. Unfortunately, under field conditions, the effect of any one factor, or combination of factors cannot be isolated since several changes are occurring simultaneously, and cannot be controlled. For this reason an invitro study of the relationship between water column bacterial decline and environmental conditions was initiated in October, 1989. The study was designed to provide die-off information from controlled laboratory experiments, which would aid in the interpretation of field data collected by the Conservation Authorities.

Laboratory experiments have been used previously to determine the effect of various factors on bacterial die-off. In this study, the effect of water temperature and chemical parameters such as: Dissolved organic carbon (DOC), total kjeldahl nitrogen (TKN), nitrates (NO_3), nitrites (NO_2), ammonia (NH_4), and phosphates (PO_4) was assessed using small aquaria and membrane diffusion chambers containing cultures of indicator bacteria.

METHODS

The control cultures of E. coli (EC) and *P. aeruginosa* (PSA) used in the experiments were isolated weekly from cow faeces and sewage. Broth cultures of EC and PSA were centrifuged, and diluted 10 fold to a concentration of 10^3 in filter sterilized well water prior to injection into the chambers.

The well water had been selected, based on chemical test results, as a clean source, exhibiting low to trace levels of the various chemical parameters. Filter sterilization using a 0.2 micron Millipore filter was found to be preferable to autoclaving the water, as this latter method results in a delayed die-off effect (Harris and Walters, 1989).

Commercial 5 gallon aquaria were installed in large incubators, and filled with 9 litres of filter sterilized well water. The tanks were continuously aerated during the experiments by pumping air into the water via plastic tubing connected to aquarium pumps.

Both control and test tanks were used for each experiment. Test tanks were prepared by increasing concentrations of individual chemical parameters, such as DOC or NO_x to levels observed in fresh water streams receiving variable pollution impacts. This was accomplished by adding pre-calculated amounts of appropriate media such as manure or sodium nitrate to the tanks. Control tanks contained only filtered well water.

Fresh water and chemicals were added to the tanks every 2 days during the experiments. The tank water was sampled for chemical analysis at the start of each experiment, after each water change, and at the end of the experiment. Samples were submitted to the Ministry of the Environment (MOE) for analysis of all the test parameters, as well as, conductivity, turbidity, and pH.

For the water column experiments, triplicate diffusion chambers were filled with the diluted EC and PSA suspensions, and then placed into the aquaria. Separate chamber sets were used for each control, as PSA is somewhat inhibited by the presence of EC in diffusion chambers (Harris and Walters, unpublished data). Bacterial concentrations were measured over a six day period by daily withdrawing 3 mL samples from the chambers, and analyzing these by membrane filtration for EC and PSA. All analyses were performed according to MOE methods.

Four replicate experiments examining the effect of different DOC concentrations on bacteria survival were run at 3 temperature regimes: 4°c, 10°c, and 20°c. Triplicate tests assessing the effect of other chemicals on survival were run at 20°c only.

In sediment survival experiments, chambers were filled with 50 grams of a filter washed mixture of fine sand and bentonite clay, and then inoculated with 5 mL of the diluted EC or PSA culture. Inoculated chambers were then placed in the aquaria . Only the effect of increased DOC on sediment bacterial survival was determined by duplicate experiments at 10°c and 20°c. The experiments were conducted over a 10 day period by daily removing chambers and analyzing the sediments for EC or PSA using MPN procedures specified by the MOE.

Data from the survival runs was analyzed by statistical tests. Bacterial survival rates were computed by linear regression analysis of the bacterial concentration in each chamber with time. Comparison of the die-off rates between control and test groups was performed by single factor anovar analysis. The relationship between water column bacterial survival, water temperature and DOC was also assessed by linear regression analysis.

RESULTS

Water column and sediment bacterial die-off rates determined under different temperature and chemical treatments are presented in Figures 1 and 2. The rates shown are a geometric mean average of data from all runs. Test groups 1 (Figs. 1 and 2) refer to experiments utilizing moderate increases in the various chemicals, while test groups 2 denote experiments examining the effect of large increases.

As seen in Figure 1, the die-off rate of EC in the control tanks was found to increase with increasing water temperature. Regression analysis of EC die-off with temperature showed a significant, but not strong positive correlation ($r = +.584$). Elevating DOC levels in the water counteracted the effect of temperature, causing die-off to decrease dramatically (Fig. 1). EC die-off rates showed a strong negative correlation with DOC ($r = -.705$). However, anovar analysis revealed that significant differences in the die-off rates between control and test DOC tanks occurred only at 20°c (5% probability level).

PSA in contrast, exhibited an elevated survival response to increasing temperature ($r = -0.734$). Previously, this organism was found to grow in well water at temperatures of 15°c or higher (Harris and Walters, unpublished data). Increasing DOC levels accentuated this growth response. Significant differences in die-off rates between control and test tanks occurred at all three temperatures.

Magnifying the concentration of NH_3, NO_3, TKN, and PO_4 in aquaria water at 20°c, produced almost no effect on the die-off rates of EC (Fig. 1). Residual chloride caused a decrease in die-off when increased moderately possibly due to the establishment of more favourable osmotic conditions for the organism. Elevating NO_2 concentrations resulted in an increased die-off response. NO_2 may be slightly toxic to the organism at high levels, and under these conditions.

PSA die-off rates varied in response to elevated NH_3, NO_3, NO_2, TKN, and PO_4 (Fig. 1). Die-off was not observed in the NH_3 and NO_2 control and test tanks. Invitro PSA die-off response is variable at 20°c, and it is not uncommon for regrowth to occur. However, the regrowth of PSA in the NH_3 test tanks was more pronounced than in the control tanks. Increasing levels of TKN and PO_4 appeared to cause a decrease in die-off, while elevating residual chloride levels had no effect. Anovar analysis of the data from these experiments did not detect any significant differences in the die-off rates between control and test tanks despite these observed trends.

Both EC and PSA exhibited somewhat increased die-off rates in sediments under elevated DOC conditions (Fig. 2). This observation is not supported by field die-off data. Unfortunately, anovar analysis could not be performed on the sediment survival data due to lack of sufficient replication. It is therefore difficult to determine if the observed increases in die-off were significant.

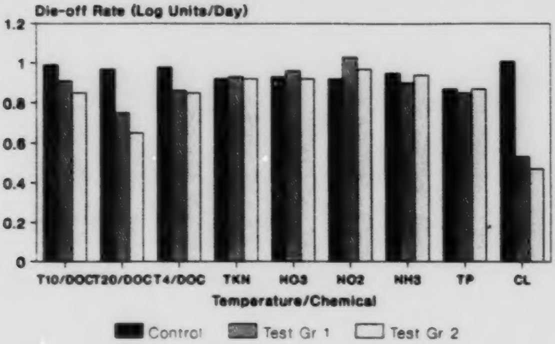
Adsorption of the bacteria onto the clay may be affected in some way by the increased DOC content, through changes in pH or the surface charge of the clay particles. Whether the affect is increased adsorption, leading to reduced bacterial recovery and a false die-off effect, or decreased adsorption, resulting in a loss of the clay's protective action, is unknown, and beyond the scope of this study.

CONCLUSIONS

Bacterial survival response is heightened by elevated levels of DOC in water. The survival phenomenon is most pronounced at warmer temperatures, but occurs under colder conditions as well. Reducing inputs that cause increased DOC levels in streams may help to increase bacterial die-off, and thereby lessen the biological pollution impact on downstream areas. DOC analysis should be included in routine monitoring tests.

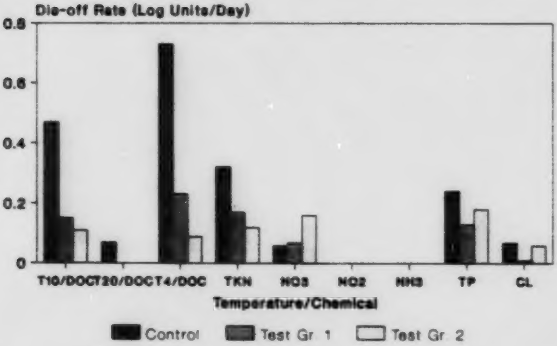
Figure 1

THE EFFECT OF TEMPERATURE AND NUTRIENTS ON E. COLI SURVIVAL



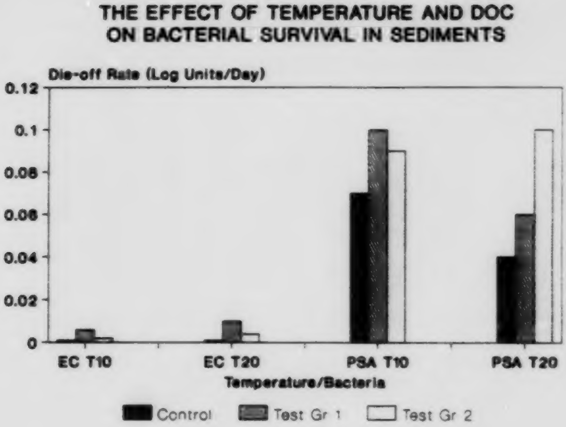
T = Temperature in degrees celsius
NO3/NO2/NH3/TKN/TP/CL = 20 degrees C

THE EFFECT OF TEMPERATURE AND NUTRIENTS ON P. AERUGINOSA SURVIVAL



T = Temperature
NO3/NO2/NH3/TKN/TP/CL = 20 degrees C

Figure 2


THE EFFECT OF TEMPERATURE AND DOC
ON BACTERIAL SURVIVAL IN SEDIMENTS
Die-off Rate (Log Units/Day)
0.12
0.1
0.08
0.06
0.04
0.02
0
EC T10
EC T20
PSA T10
PSA T20
Temperature/Bacteria
Control
Test Gr 1
Test Gr 2

BP7

THE EFFECT OF FARM LIQUID WASTE APPLICATION ON RECEIVING WATER QUALITY

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Previous studies by the Ausable Bayfield Conservation Authority (Balint 1985) and the Ontario Ministry of the Environment, Southwestern Region (O.M.E. 1984) established that in some cases the land application of liquid manure causes bacterial and chemical contamination of field tile drains. The effluent from those tile drains may result in contamination of receiving streams and ultimately beach closures. The primary objectives of this current study are to determine how soil structure, soil moisture and rate of application influence the impact of land application of liquid manure on tile drain water quality.

Previous research on bacterial movement through soil columns, including studies by Gerba *et al.* (1975), Smith *et al.* (1972), and McCoy (1969), indicated that soil was an efficient filter for bacteria. On the contrary, and in support of this study, Evans and Owens (1972) found a 30-900 fold increase in fecal bacteria concentration in the tile effluent from a sandy clay loam pasture field within two hours of spreading liquid manure. A one time observation by Patterson *et al.* (1974) found the water from 1.5 m deep drains in a plowed field to be cloudy and foul smelling within 30 minutes after a 5mm (50,000 Lha^{-1}) application of liquid manure.

Thus far, 11 liquid manure spreading events have been monitored on a total of 5 different soil types, under a variety of field conditions, in Huron and Perth Counties, Ontario. Table 1 gives a summary of each of the manure spreading events including the rate of manure application, a brief description of the field conditions and changes in bacterial water quality. Participating farm operators and/or custom applicators were requested to spread the liquid manure as they would normally. The irrigation method of spreading was used for 10 of the manure applications, while a tank spreader with manure broadcast on the ground was used for the remaining one. Changes in the concentrations of bacteria and nutrients in the soil underlying the area of manure application were monitored in addition to changes in the tile drain water quality. Bacterial parameters tested for in the manure, tile drains and soil included, fecal coliform, fecal streptococcus, and *Escherichia coli*. For 9 of the manure applications the biotracers; nalidixic acid resistant *Escherichia coli* (E.C.(N.A.)) and rifampicin resistant *s. faecalis* (F.S.(R.I.F.)), were introduced with the liquid manure to trace bacterial movement in the soil and water. These biotracers are easily detected in water and soil and are not normally present in the natural environment.

For 7 of the 11 manure spreading events (numbers 1, 3, 5, 8, 9, 10, and 11) (see Table 1) water quality degradation was observed within 2 to 7 hours following the initiation of spreading. It is believed that soil macropores provided pathways for the manure to travel to the tile drains. Soil moisture is also believed to have played a role since contamination of tile drains only occurred when there was some tile flow prior to spreading. Event numbers 2, 4, 6, and 7 experienced little or no contamination of the tile drains. For numbers 2 and 4, low levels of contaminants were present when tile flow resumed. For #6 little contamination of

Table 1: Summary of Each of the Manure Application Runs

Event #	Date	Soil Type	Tile System and Spacing	Crop Rotation	Ground Cover and % Residue*	Tile Flow	Rate of Application L ha^{-1}	Comments
1	May '89	Perth clay loam	systematic 15 m	corn/bean/ wheat	fall plowed 6%	Yes	76,500	- 3400 fold increase in bacti. conc. in 2 hours
2	Aug '89	Perth clay loam	systematic 15 m	corn/bean/ wheat	wheat stubble 95%	No	140,700	- contamination (low) delayed until tile flow resumed
3	Sept '89	Perth clay loam	random	corn/barley /hay	corn silage stubble 57%	Yes	93,000	1600 fold increase in bacti. conc. within 4 hours
4	Oct '89	Brookston clay loam	systematic 15 m	soybean/ corn	soybean residue 76%	No	56,000	- contamination (low) was delayed until flow resumed
5	Nov '89	Wauseon sandy loam	systematic 15 m	soybean/ corn	soybean residue 78%	Yes	54,000	- 1000 fold increase in bacti. conc. within 6 hours
6	May '90	Listowel silt loam	systematic 15 m	soybean/ corn	fall plowed 6%	Yes	36,000	- 200 fold increase in bacti. conc. within 5 hours
7	Jun '90	Perth clay loam	systematic 15 m	corn/bean/ wheat	seed bed prepared 1%	Yes trickle	111,000	- slight increase in bacterial concentrations but not significant
8	Jul '90	Perth clay loam	random	hay/corn/ grain	hay 93%	Yes V.High	100,000	- 30 fold increase in bacti. conc. within 20 minutes
9	Aug '90	Perth clay loam	systematic 15 m	corn/bean/ wheat	wheat stubble 94%	Yes trickle	106,000	- 45,000 fold increase in bacti. conc. in 2.5 hours and increased tile flow
10	Sept '90	Listowel silt loam	systematic 15 m	corn/bean/ wheat	wheat stubble 94%	Yes trickle	44,300	- 30,000 fold increase in bacti. conc. and increased tile flow
11	Sept '90	Huron clay loam	systematic 15 m	corn/bean/ wheat	wheat stubble 96%	Yes	72,000	- 1,000 fold increase in bacti. conc. in 2 hours

the tile drains occurred on the day of spreading, however, after a 15 mm rainfall the following day, the tile drains were contaminated. In #7, in which no significant contamination resulted in the tile drain water, manure was spread on ground that was recently prepared for seeding of white beans. This cultivation may have destroyed the continuous root or pore channels in the surface soil horizon.

At each manure application site, soil bacteria, including the biotracers, were measured in the soil profile at three depths: 0-10 cm, 30-35 cm, and 45-50 cm (1989), 70-75 cm (1990). Figure 1 shows the concentration of both fecal coliform bacteria and the introduced (FS(RIF)) bacteria at various depths in the soil, before and after spreading, expressed as # of bacteria per 100 g of soil. This profile, which is from event #2 is typical of other events, with the exception of #7 where there was virtually no movement of bacteria through the soil column. Biotracer results confirmed that contamination from the spread manure reached the tile drain water. Figure 2 shows tile drain concentrations of fecal coliform and the introduced (FS(RIF)) over time for one of the spreading events.

Figure 1. Soil Bacteria Concentrations
Event #2 - August 1989

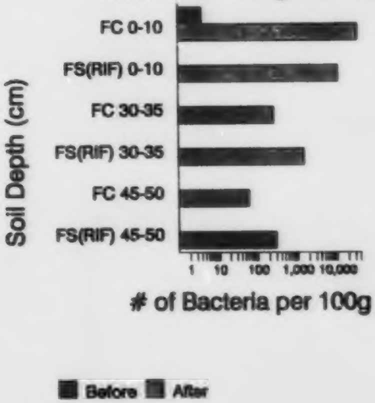
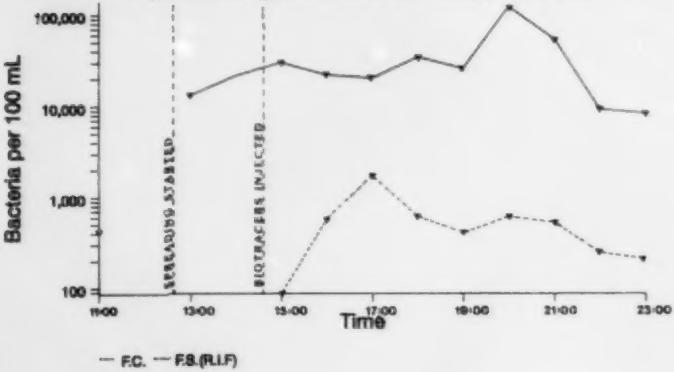


Figure 2. Drain Bacteria Concentrations
Spreading Event #8 - July 9, 1990



It appears that the four major factors influencing the impact of land application of liquid manure on tile drain water quality are; the presence of established continuous macropores (root/animal channels and structural cracks), tile drain flow at the time of spreading, rainfall shortly following manure application, and the rate of application.

This study was subject to some scheduling difficulties in 1989 and 1990 due to weather and crop stage. It is anticipated that manure spreading events will be monitored two more times in 1990. Future research should focus on the impact of tillage prior to manure application since macropore flow appears to be the dominant factor in the transport of manure to tile drains.

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* Percent Residue Cover - A 30.5 m rope with markings every 30.5 cm is laid diagonally to the direction of cultivation. The percent residue is determined by counting the number of times that residue is present at the 30.5 cm markings. The minimum residue size is 3.8 cm by 0.3 cm.

DP6

STATISTICAL ASSESSMENT OF MULTIVARIATE ORDINATION TECHNIQUES FOR ZOOBENTHIC COMMUNITIES AND WATER CHEMISTRY FOR LAKES FROM CENTRAL ONTARIO. Donald A. Jackson* and Harold H. Harvey, Department of Zoology, University of Toronto, Toronto, Ontario M5S 1A1

Researchers studying ecological communities or environmental impact assessment frequently must assess data sets comprising large numbers of sampling sites, species, and environmental variables. The large number of pairwise comparisons of variables makes the use of simple correlation analysis of limited use. With increasing frequency, researchers employ some method of multivariate statistical technique such as principal component analysis (PCA) or cluster analysis. Many of these methods are applied indiscriminantly without regard for the underlying assumptions of the methods and the characteristics of the data. For example, water chemistry variables are often non-linearly related yet researchers use methods requiring linear relationships (e.g. PCA, canonical correspondence analysis). The implications of using these methods are still poorly recognized.

When using any of these methods, an underlying assumotion of the techniques is that there are non-random patterns among the sites or variables. Multivariate analyses are used to summarize these methods into a reduced number of dimensions. Unfortunately, with field-collected data, the dimensionality of the patterns is unknown. It is important to recognize the dimensionality of the data otherwise one risks discarding important information associated with unutilized multivariate components or interpreting nonsignificant components as being important. We are examining various traditional measures of assessing the dimensionality as well as developing alternative methods employing bootstrapping (statistical resampling) techniques.

More comprehensive measures of the concordance between ecological communities and their corresponding environmental conditions are being developed. Traditional approaches have included correlating community-based multivariate axes with environmental variables (again leading to excessive numbers of correlations and the associated inflated Type I error) or methods such as canonical correlation analysis which assume linear relationships among and between the species data and the environmental data. We have developed a multivariate measure testing the concordance between benthic invertebrates, fish species compositions, water chemistry, lake morphometry, and spatial arrangement. **PROTEST** is a multivariate **PRO**crustean **TEST** based on a least-squares measure of the goodness-of-fit between two data sets with the subsequent probability determined using a randomization test. The rationale and use of **PROTEST** will be discussed in our presentation.

BP9

GEOCHEMICAL ALTERATION OF ROAD DE-ICING CHEMICALS BY SUB-SURFACE ROCK-SOIL-WATER INTERACTIONS.

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Introduction

Road de-icing chemicals are one of the most serious causes of groundwater pollution in Canada. Applied to roads and highways throughout southern Ontario and many other Canadian Provinces, the chemicals (NaCl and $CaCl_2$) are easily mobilized by rain and meltwaters. As a result, typically 50% of annually applied road de-icing chemicals are flushed from the catchment by surface waters, with the remaining 50% infiltrating slowly through the unsaturated zone to the water table where it threatens to cause widespread degradation of groundwater quality. An ongoing study by the Groundwater Research Group at the University of Toronto plans to develop a series on numerical models that will predict the environmental fate of these chemicals and thereby recommend procedures that will minimize environmental impact.

While the predictive models should deal adequately with the fate of the chemically conservative chloride ion, the predicted behaviour of Ca and Na will depend on a knowledge of the interactions between these ions and the shallow sub-surface soils and sediments. Soil water in the unsaturated and saturated zone is usually in equilibrium with the ions adsorbed on the soil particles and organic matter. As precipitation or run-off infiltrates through the soil, its composition changes to reach equilibrium with the soil by exchange between the adsorbed and free water ions. When road salt laden waters enter the soil during winter or early spring, the sodium ion, which is the dominant cation species, exchanges with the cations adsorbed in the soil (mainly calcium). By the time infiltrating water reaches the water table, its original cationic composition will have been changed by a series of soil-water interactions, the magnitude of the change depending on the soil or rock type, the thickness of the unsaturated zone and the chemistry of the preceding infiltrating waters. During the summer, repeated infiltration of salt-free water will reverse the exchange process and remove the weakly adsorbed sodium, to near background concentration levels. Studies in Britain showed that sodium adsorbed during winter salting was removed from the upper 50 mm of roadside soils prior to the onset of the following winter (Thompson, et. al. 1986)

Below the water table the equilibrium chemistry of salt-laden and salt-free waters will continue to evolve, influenced by the ion exchange equilibrium. Studies in a road salt contaminated shallow aquifer by Killey and Devgun (1987), identified changes in the chemistry of a salt plume. Near the source of the plume, calcium concentrations were at background levels but sodium was much higher (Na:Ca ratio approximately 3). Further downgradient, the equilibrium had changed to achieve a Na:Ca ratio of 1, typical of background waters. However, both sodium and calcium concentrations were now above background levels.

Laboratory Experiments

Current research described here is addressing the role of rock-soil-water interactions on modifying the chemistry of the infiltrating waters through a series of laboratory experiments. Two types of experiment are being carried out, both involving salt solutions prepared by dissolving commercially available road de-icing salts in simulated precipitation. For both types of experiments, cation exchange capacity and exchangeable cations are determined respectively by using sodium acetate and ammonium acetate saturation to extract ions, and by using atomic absorption/flame emission to analyse for the major cations. In the first type of experiment, batch tests are being performed using sandy and silty soils with varying organic content, clay content and carbonate content. Soil samples are saturated alternately with salt solutions at varying concentrations and with simulated rainfall. The supernatant is collected and analysed for major ions. Exchangeable major cations are determined for the treated soil. The ratio of Na:Ca occupying exchange sites is determined for different treatments.

The other type of experiment uses a simple soil column to examine the changes in water chemistry and adsorbed cations resulting from infiltration of salt water through an unsaturated soil. Soil cores, averaging 80 cm in length, are obtained from an urban park, by hammering 55 mm diameter acrylic tubes into grassed alluvial soils. Except for some minor compaction, the soil cores, when visually compared with the soil profile exposed in an adjacent test pit, are relatively undisturbed. Table 1 lists the properties of the soils used in the first infiltration series. The soil is a silty fine sand grading into a medium sand below 0.85 m. The B horizon is enriched in clay (15% ave. versus 9% ave. and 3% in the A and C horizons respectively). In the laboratory, the soil core was infiltrated with a series of 250 ml aliquots of simulated rainfall containing either no salt or salt at various concentrations. The composition of the aliquots was designed to imitate the pattern of a soil receiving road run-off during the salting season and shortly after. The core was gravity drained, and each infiltration event took 36 - 48 hours to complete. The effluent from each infiltration event was analysed for major cations to examine changes in the infiltrating water. At the conclusion of the infiltration series, the soil core was extruded and sampled in 60 mm sections. Each section was sub-sampled, from the centre, edge, and across the column to identify any channelling during infiltration. (No channelling was visible during infiltration; the wetting front advanced relatively uniformly down the column.) Moisture contents were measured. Exchangeable major cations were determined for 12 representative samples and compared with ratios of exchangeable ions prior to testing.

Experimental Results

The experimental results reveal that the cationic constitution of the road salt solutions can be significantly altered by rock-soil-water interactions. Most significantly these changes take place in the organic soil A horizon. The B and C soil horizons contribute less actively to the cation exchange process. The experimental results are consistent with the basic exchangeable cation characteristics of the shallow soils and sediments; the findings are also consistent with the chemical character of groundwaters known to be contaminated by road de-icing chemicals.

Table 1 Soil Properties - Soil Core Sampling Site

Horizon	Zone	Depth m	Texture	Organic Matter wt. %	Ratio Exchangeable Na:Ca
A	A1	0 - .21	silty sand	4.7	0.01
	A2	0.21 - 0.38	silty sand	3.8	0.01
B	B1	0.38 - 0.45	clayey silty sand	1.7	0.03
	B2	0.45 - 0.59	clayey silty sand	2.2	0.04
C		0.59 - 0.85	silty sand	0.6	0.1

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BP10

STANDARDIZED REARING MATERIALS AND PROCEDURES FOR HEXAGENIA, A BENTHIC BIOASSAY ORGANISM: COMPARISON OF SEDIMENT TYPES

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ABSTRACT

All life stages of the aquatic mayfly Hexagenia have been used extensively for biomonitoring/bioassay applications. However, use of larvae for toxicokinetic studies and bioassay procedures is limited by lack of standardization in control sediments. A synthetic medium suitable both for rearing and for laboratory contaminant assessment must 1) promote high larval survival and rapid growth; and 2) be free from contaminants of concern.

To characterize sediments most suitable for larval growth, we collected sediments from six field sites: Anchor Bay, Lake St. Clair (ANC); Balsam Lake (BAL); Cook's Bay, Lake Simcoe (COO); Honey Harbour, Georgian Bay (HON); Lake Nicolet, St. Marys River (NIC); and Saginaw Bay, Lake Michigan (SAG). A synthetic laboratory standard (STND) sediment (2:1 dry wt. potting soil:potters clay) previously used for successful rearing (<20 % mortality) was compared to field samples. All sediments were dominated by silt/clay. Organic content ranged from 2 % (ANC and NIC) to 28 % (STND).

One-day old larvae were inoculated into growth tanks (7 larvae per 63 cm^2 tank) containing one of the 7 sediment types for 90 d and until adult emergence (n = 5 replicates/ sediment type/ time trial). Mean head width (HW) and relative mortality were determined for each tank. After 90 d growth, larval survival in SAG, NIC, COO and STND (55-85%) was significantly higher than in ANC, BAL, HON and SAG (25-55%) sediment ($P< 0.01$). Larvae grown in HON and SAG sediments had attained the largest size. BAL, STND and ANC sediment supported the smallest larvae ($P < 0.001$). Other trials that rear larvae to emergence are still in progress.

Two larval substrate preference experiments were conducted. Blocks of the 7 sediment types were placed in an aquarium to form a grid of 49 cells. Eight larvae/ cell were added and allowed to move freely among cells. After 7 d, SAG, ANC, COO and HON contained significantly more larvae then other sediments ($P < 0.001$). STND sediment harboured the fewest larvae.

Since Saginaw Bay sediment is the most conducive to growth and survival of larvae, we are altering constituents of our standard sediment using diatomaceous earth, potter's clay and potting soil to more closely mimic the preferred sediment. The general utility of synthetic sediment in bioassay procedures is being examined by comparing responses of Hexagenia larvae in the standard sediment to growth in field-collected contaminated sediment.

1. INTRODUCTION

Larvae of *Hexagenia* mayflies are important field and laboratory test organisms. They have been recommended as a standard for evaluating toxic effects of contaminated sediments (International Joint Commission 1987; Lomas and Krantzberg 1988). These organisms are a common food source for many fishes and thus may play a significant role in contaminant transfer from sediments to other trophic levels. *Hexagenia* have been used extensively for biomonitoring/bioassay applications in egg (Friesen 1979), larval (Fremling 1967; Henry et al. 1986; Bedard 1990) and adult (Kovats and Ciborowski 1989) developmental stages. However, use of *Hexagenia* for toxicokinetic studies, bioassay procedures and field biomonitoring is limited by lack of standardization in control sediments and availability of test animals.

Various sediment bioassay and biomonitoring techniques assume that variation in test organism survival, growth and/or ultimate contaminant burden directly reflect the concentration and toxicity of contaminants in the sediment. Response differences between contaminated and uncontaminated site-collected treatments (sediments) presumably reflect the influence of the contaminants alone. We propose that comparing these treatments with a culture-sediment control permits one to ascertain the extent to which on-site sediment effects result from inappropriate or suboptimal physical sediment characteristics. Accordingly, we are developing protocols directed towards providing suitable standardized substrate and rearing conditions for larvae of *Hexagenia*.

The objectives of our study were to make available a continuous supply of eggs suitable for laboratory rearing, and to develop and determine the effectiveness of standard sediment and feeding regimes suitable for promoting rapid, synchronous growth of larvae of *Hexagenia*, using easily acquired materials free of organic and inorganic contaminants. In this report, we outline:

1) Collection and cold-storage maintenance of genetically consistent *Hexagenia* egg stocks from Lake St. Clair emergent populations. This material is maintained for distribution on request to individuals/organizations requiring research/assay specimens.

2) Synthesis of a sediment composed of commercially available materials of texture and composition suitable for promoting contaminant-free development of newly-hatched larvae of *Hexagenia* to maturity in the laboratory.

3) Comparison of larval *Hexagenia* growth (relative to synthesized sediment) in natural sediments from habitats especially suitable for *Hexagenia* development with growth in the synthetic sediment.

2. MATERIALS AND METHODS

2.1. Study animals and rearing conditions

2.1.1. Collection of study animals and maintenance of eggs

Eggs were collected in the summers of 1989 and 1990 from females emerging from Lake St. Clair (42°20'N 82°37'W). Adult females were collected in late June and early July using portable ultraviolet light traps (Kovats and Ciborowski 1989). Approximately 6.5 million eggs were obtained from a total of ca. 1600 female imagoes in each year. Taxonomic analyses of males collected at the same time suggest that approximately 67 percent of imagoes were *H. limbata* (Serville) and 33 percent were *H. rigida* McDunnough (n=250). Adult females cannot be identified to species.

Eggs from groups of 20 or more females were amalgamated into polyethylene bags containing aerated, distilled water. All eggs were cooled in a stepwise fashion to 8°C in 4°C decrements (Friesen 1981) and stored to provide a year-round supply of stock material.

To evaluate the possible influence of overwintering eggs on delayed recruitment into natural populations, the effect of cold storage was examined. Eggs collected in 1989 were used to estimate viability and to determine whether a proportion of eggs required a period of cold-storage prior to hatching that may contribute to subsequent size variation observed in natural larval populations.

At the time that eggs were returned to the laboratory after collection, batches of approximately 100 eggs were removed from their bags. Half of the eggs (n=50) were placed in covered petri dishes at room temperature while the other half were cooled to 8°C in 4°C decrements and stored under refrigeration. The eggs kept at room temperature were monitored daily for two weeks. As larvae hatched, they were removed from the petri dish and enumerated. The unhatched eggs were then left at room temperature and examined every few days for two months (D. Giberson, University of Manitoba, pers. comm.). At the end of this period (12 Sept 1989) they were placed into cold storage (8°C). On 11 January 1990, these eggs, in addition to the eggs originally put in cold storage were warmed to room temperature to monitor hatch over a further 3 month period.

2.1.2. Larval rearing conditions

Animals were reared in containers under laboratory conditions as outlined by Hanes (1989). Two-L glass jars (Lomas and Krantzberg 1988) are equally suitable containers. One-day-old larvae were inoculated into appropriate sediments and maintained at densities and feeding schedules previously determined to maximize growth and survival (Hanes and Ciborowski 1989). Rearing chambers consisted of either 500-mL or 1-L styrofoam or plastic tubs (7 larvae 63 cm^{2} = 1000 larvae m^{-2} ; Hanes 1989) or 2-L glass jars (Lomas and Krantzberg 1988). Containers were aerated using the multiple-bank system of Corkum and Hanes (1989). Lighting was provided from incandescent and fluorescent sources, timer-regulated to correspond to a 16:8 L:D photoperiod. All rearing chambers were maintained at room temperature (21-24° C). This temperature produces higher survival rates and greater size at maturity among laboratory-reared specimens than other temperatures (Wright and Mattice 1981a). Values of dissolved oxygen, conductivity and pH were monitored at regular intervals throughout all experiments. Larvae were fed an aqueous mixture of ground Tetramin ® fish food, aflalfa flour and baker's yeast (modifed from M.G. Henry, Univ. Minnesota, pers. comm.) applied to the water surface as an aerosol every 3-4 days (20 µg dry wt./cm^2/d ; Hanes, 1989).

2.2. Artificial sediment synthesis

Previous workers evaluating growth, behaviour and ecotoxicology of burrowing mayflies have used locally collected natural sediments from purportedly uncontaminated regions (Landrum and Poore 1988, Bedard 1990). M. Friesen (pers. comm.) proposed using plant potting soil as a rearing medium for *Hexagenia rigida* larvae. M. Henry (pers. comm.) found that *Hexagenia limbata* grew well in sediments composed of a mixture of potting soil and Lake St. Clair clay. We previously achieved excellent rearing success (>90 percent survival) using a mixture of 2 parts potting soil and 1 part potter's clay (ratios based on dry weight) (Hanes and Ciborowski 1989).

Potting soil (Zehr's "No Name" Potting Soil®) was air dried and passed through a No. 10 (1-mm) sieve to remove large clumps of organic material. An appropriate (moisture corrected) quantity of Terra Cotta potter's clay was mixed with distilled water in a blender to produce a thick slurry. The slurry was mixed with the sieved soil until a homogeneous mixture was obtained. The wet sediment was air-dried until damp and was then passed through a No. 5 sieve (2-mm) to produce an easily manipulated, coarse-powdered sediment that was allowed to air dry to constant weight at room temperature. Dried sediment was stored covered at room temperature, and autoclaved (20 min at 240° F, 15 PSI) prior to use.

2.3. Comparison of natural and synthetic sediments

2.3.1. Collection of natural sediments

Suitability of the synthetic sediment was assessed by monitoring survival and larval size after 90 d of rearing newly-hatched *Hexagenia* larvae (Hanes 1989) and by choice chamber experiments (Wright and Mattice 1981b). We compared *Hexagenia* development in the synthetic sediment with sediments from habitats known to be presently or historically suitable for *Hexagenia* development.

We collected natural sediments from six sites; Lake St. Clair (Anchor Bay, ANC); Balsam Lake (BAL); Lake Simcoe (Cook's Bay, COO); Georgian Bay (Honey Harbour, HON); St. Marys River (Lake Nicolet, NIC); and Lake Michigan (Saginaw Bay, SAG) (Table 1). Of these sites, the MOE frequently collects benthos for biomonitoring/bioassay at Honey Harbour (*Hexagenia*) and Balsam Lake (*Elliptio* mussels). The remaining four sites have historically supported large populations of *Hexagenia*.

Table 1. Summary of Sediment collection for 1989. The occurrence of *Hexagenia* larvae at the site at the time of collection is indicated.

Location	Code	Coordinates	Date (1989)	Amount (L)	*Hexagenia*
Honey Hbr., ON	HON	44° 50' N 88° 25' W	27 Aug	45	present
Balsam L., ON	BAL	44° 35' N 79° 49' W	27 Aug	45	present
Cook's Bay, ON	COO	43° 15' N 78° 29' W	28 Aug	45	absent
L. Nicolet, MI	NIC	46° 23' N 84° 15' W	17 Sept	45	present
Saginaw Bay, MI	SAG	44° 00' N 83° 40' W	17 Sept	45	absent
Anchor Bay, MI	ANC	42° 35' N 82° 44' W	20 Sept	25	present

At each of the six locales, sediment was collected using a mini-ponar grab (20 cm x 20 cm). *Hexagenia* and/or *Chironomus* (Diptera: Chironomidae) larvae occurred and were removed from the sediment in all samples. Sediment was returned to the laboratory in 15-L plastic buckets, autoclaved, and placed into cold storage (4° C).

2.3.2. Sediment composition

The particle size distribution of sediment samples (natural sediment from six sites + standard) was estimated by wet-sieving (coarse particle fraction) and hydrometry (silt and clay fractions; ASTM 1981). Mean organic matter content (4 replicates per sediment type) was determined by loss on ignition (550° C, 4 h) of oven-dried samples (105 °C, 24 h).

Both natural and synthetic sediments were similar in inorganic particle size distribution but differed in organic content. All sediments consisted of 30-60 percent silt and 30-50 percent fine sand. The standard sediment had the greatest amount of organic material (ca. 28%), whereas sediment collected from Anchor Bay and Lake Nicolet had the least organic material (ca. 2%) (Table 2). Texture of organic materials differed between natural and the artifical sediments. Synthetic sediment contained primarily leafy and woody material characteristic of a littoral aquatic sediment. The natural sediments were dominated by fine, amorphous organic material typical of profundal regions.

2.4. Comparison of larval growth among sediments

The seven sediment types (see above) were each placed in standard rearing chambers and inoculated with newly-hatched *Hexagenia* larvae [natural sediments from 6 sites + standard sediment x 5 replicates/ treatment = 35 trials for 2 time periods (90 d, time to emergence)]. A density of 7 larvae per rearing chamber (1,000 larvae m^{-2}) was selected. This density allows rapid growth and low mortality while normally providing enough larvas for analysis of intrareplicate variability (Hanes and Ciborowski 1989).

Larvae were harvested from the appropriate containers after 90 d and preserved in 70% ethanol. Relative survival (proportion) was tabulated for each tank. Head width (HW), measured across the eyes, was determined for all larvae using an ocular micrometer in a dissecting microscope.

One-way analysis of variance (ANOVA) was used to test for differences in larval survival and size among the sediment types. If significant differences occurred, a Student-Newman-Keuls (SNK) multiple comparison test was used to determine which groups differed from one another.

Table 2. Mean (and 1 S.E.). amount of organic matter (percent) occurring in four replicate samples of each sediment type.

	Sediment Source						
	Anchor	Balsam	Cook's	Honey	Nicolet	Saginaw	Standard
Organic Content	2.38 (0.096)	18.55 (0.772)	11.94 (0.131)	4.09 (0.247)	2.14 (0.761)	8.89 (0.086)	28.21 (0.176)

2.5. Sediment preference

Two replicate seven-day sediment choice experiments were conducted to provide a measure of larval substrate preference. The choice-chamber was a 20-cm deep 56 x 56 cm plexiglass aquarium. An aluminum partitioning grid consisting of 49 (i.e. 7 x 7) cells (8 cm x 8 cm x 10 cm high) was placed within the square plexiglass aquarium. Seven aliquots of each sediment type (six field-collected sediments and standard sediment) were placed within the aluminum grid in a Latin Square configuration. Each sediment type was represented only once in a given row and in a given column of a grid of blocks so that no two blocks of the same sediment type were adjacent. The arrangement of the sediment was changed between replicates such that all combinations of adjacent sediment types were examined. The sediments had been kept in cold storage for approximately 18 weeks at the time the experiment began.

Approximately 250 mL of sediment was added to each cell (ca. 5 cm depth). Aerated, distilled water was added to the tanks to produce a depth of 13 cm over the sediment). One mL of concentrated food mixture was added to each cell and stirred into the sediment. The aquarium was aerated for one week prior to addition of larvae (Hanes 1989).

Test organisms had been reared in the standard sediment at a density of 8 larvae per 63-cm^2 rearing chamber (1270 larvae m^{-2}) for six months prior to the experiment (mean length ± 1 S.E. = 12.77 mm ± 0.256, n = 382). Eight larvae were placed within each cell. The aluminum partitioning grid was removed after 1 h and replaced 7 days later (Wright and Mattice 1981b). *Hexagenia* larvae were recovered and enumerated by passing the sediments within each partition through a 500-μm sieve. Larval size (head width across the eyes) was subsequently determined.

3. RESULTS AND DISCUSSION

3.1. Viability and variation among hatching eggs

Approximately 90 - 95 % of all eggs hatched whether or not they were previously placed into cold storage. Eggs maintained at room temperature immediately after collection began to hatch after 14 days. Cold-stored eggs required 6 d at room temperature prior first hatching. Almost all hatching occurred over a 4 d interval regardless of storage method.

Of the eggs that were refrigerated after having been left to hatch at room temperature, very few additional hatches were observed (< 0.01%). Therefore, it appears that delayed recruitment by overwintering plays a minor role in natural populations at this latitude (42° 20'N). However, at more northern latitudes, it has been suggested that overwintering of eggs may be an important source of delayed larval recruitment (D. Giberson, pers. comm.).

In addition to providing us with adequate material for experimental rearings, the eggs collected from adult females are available for distribution to other laboratories. We feel that use of eggs from a single source will minimize test organism response variability among laboratories.

3.2. Larval growth and survival

After 90 d growth, survival significantly differed among the seven sediment types (ANOVA, $p < 0.01$). The Student-Newman-Keuls (SNK) test detected significant differences between two groups of sediment (Figure 1A). Although there was overlap in larval survival between the two groups, survival in SAG, NIC, COO and STND was significantly higher (60-90%) than survival in ANC, BAL, HON and SAG sediment (25-30%; $p<0.01$).

Larval size did not differ among the sediment types when mean HW for all larvae within a replicate tank was used for analysis ($F_{[6,19]} = 2.439$, $0.10 > P > 0.05$). However, loss of replicates per sediment type often resulted from high larval mortality. Complete larval mortality occurred in several tanks owing to chironomid infestations shortly after inoculation with Hexagenia larvae. The lost replicates substantially reduced the power of the analysis. Accordingly, the data were reanalyzed using individual HW of all larvae that survived within a particular sediment. Because there was significant variance added among replicates within treatments (nested ANOVA, $p < 0.05$) the pooling of larvae from different replicate tanks is not strictly valid. However, this procedure revealed strong differences in larval size among sediment groups (ANOVA, $F_{[6,90]} = 7.026$, $p < 0.001$). A SNK test revealed the presence of four overlapping groups of sediment that varied in larval size ($p < 0.05$; Figure 1B). BAL, STND and ANC sediments supported the smallest larvae; HON and SAG supported larvae that attained the largest size - over twice that of larvae in the smallest size group.

3.3. Sediment preference

To test the null hypothesis that larvae were distributed randomly among the sediment types, a two-way (sediment x trial) analysis of variance was conducted. We found a significant effect of sediment on larval density ($p < 001$). Although there was no difference in substrate selection between the two replicate trials ($p > 0.05$), there was a significant interaction effect between sediment type and trial. Although larvae consistently selected or avoided the same substrates in both trials, the response was more pronounced in one trial than in the other. The STND sediment contained the fewest larvae

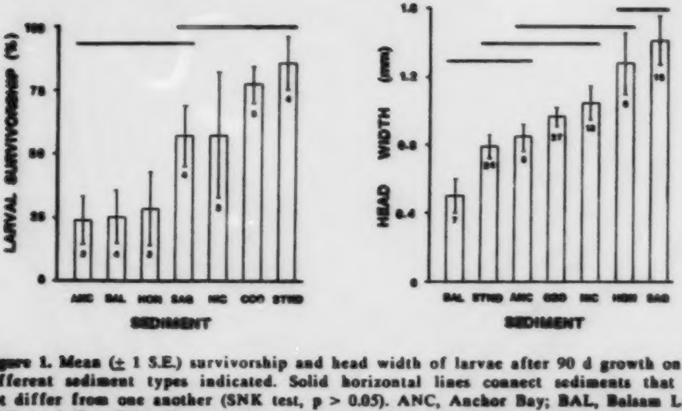

Figure 1. Mean (± 1 S.E.) survivorship and head width of larvae after 90 d growth on the different sediment types indicated. Solid horizontal lines connect sediments that did not differ from one another (SNK test, $p > 0.05$). ANC, Anchor Bay; BAL, Balsam Lake; COO, Cooks Bay; HON, Honey Harbour; NIC, Lake Nicolet; SAG, Saginaw Bay; STND, standard sediment. A. Survivorship. Numbers indicate the number of rearing tanks used in the analysis. B. Head width. Numbers indicate number of larvae used in the analysis.

(3.71±0.667/64 cm^{2}cell; Fig. 2). NIC and BAL sediment harboured significantly more larvae per cell (6.57 ± 0.746 and 7.5 ±0.769 per cell, respectively) than the STND sediment (SNK test, $p < 0.05$). The four remaining sediment types (SAG, ANC, COO and HON) contained the highest number of larvae per cell; their densities did not significantly differ from each other.

One-way ANOVA indicated that there was no significant difference in size (head width) of larvae among the sediment types ($p > 0.05$; HW=1.51±0.11 mm; body length = 12.77±0.286 mm).

Examination of larval head band patterns (D. Giberson, pers. comm.) and male genitalia (visible through the larval cuticle; Burks 1953) indicated that 90 percent of larvae were *H. limbata* and 10% were *H. rigida*. There was no relationship between preferred substrate and species identity.

Our results suggest that rearing larvae on the STND sediment results in high survivorship. However, the individuals grow comparatively slowly relative to larvae reared in natural sediments. When given a choice among sediments, larvae appear to actively avoid the artificial sediment. We speculate that slow growth and avoidance responses are largely due to the low nutritional value of the organic component of the STND sediment (woody and leaf fragments). Accordingly, we have recently modified the STND sediment through addition of diatomaceous earth and food mixture to better mimic the fine particle distribution and overall organic content of natural sediments. Of the natural sediments examined, Saginaw Bay material was the most conducive to larval growth and survival. Comparative growth studies are in progress.

Other rearing chambers are being maintained until larvae reach maturity (i.e., emergence of subimagoes is achieved). We will evaluate median time (days) to emergence and biomass (a measure of fecundity; Boerger and Clifford 1975) as indicators of sediment suitability.

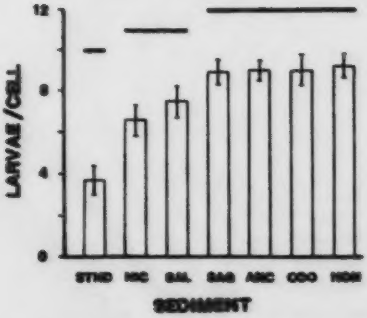

Figure 2. Mean (± 1 S.E.) number of larvae located in each sediment type within choice chamber after 1 week. Two trials were pooled for the analysis (n=14 cells per treatment). Solid horizontal lines join sediment types whose mean number of larvae do not differ from one another (SNK test, p>0.05). Abbreviations as in Figure 1.

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BP11

Tillage and Event Based Soil and Water Loss: Scale Linkages

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Soil erosion has been identified as a significant problem affecting water quality in Ontario. However, there have been few actual measurements. In addition the movement of dissolved chemicals in runoff water from agricultural land can also affect water quality. The variable, site specific nature of soil and water loss by runoff, as well as the lack of understanding of these processes under spatially varying field conditions has been documented.

Conservation tillage has been defined as any tillage system that reduces the loss of soil and water from a field. It is most often associated with minimum, non-inversion, or zero tillage systems. It is most often associated with minimum, non-inversion, or zero tillage system. The broad definition of conservation tillage is due to the recognition of significant interaction between specific soil types, climate, and tillage on runoff processes. Studies comparing one-time measurements of the effects of tillage on surface hydraulic properties may obtain contradictory results because the effects of tillage are time dependent.

Measurement of soil and water loss is difficult and is usually obtained from hillslope plots maintained over many years, or by rainfall simulation on microplots. Serious difficulties arise in attempts to transfer knowledge from laboratory or plot scale experiments to the field scale. Inability to cope with spatial variability remains a major obstacle to interpretation of research for field scale predictions.

The objectives of this study are to examine the spatial and temporal variations of soil and water loss under different tillage systems and soil types. Linkages between different spatial and temporal scales of measurement will be examined by measuring both event based losses at the plot scale, and average annual losses at the hillslope scale.

The project is being carried out on-Tillage-2000 plots. Tillage 2000 is a long term, on farm, field scale research and demonstration project initiated in 1985 by the Ont. Min. of Agric. and Food and the Dept. of Land Res. Science, Univ. of Guelph. Approximately 30 field scale sites with tillage comparisons have been established. Average annual soil loss is being measured at the hillslope scale using ^{137}Cs as a naturally occurring soil tracer.

Modified Rainfall Simulator

In order to examine the scale linkages between the plot scale ($1m^2$) and the landscape scale a modified version of the Guelph rainfall simulator was developed which allows the plot scale to be systematically increased or decreased. The new simulater system is composed of six (6) single nozzle rainfall simulators spaced evenly over a 1.6 x 10 m long plot. Each of the nozzles are connected to their own pressure regulator and solenoid control value. The pressure and solenoid switches are controlled by a single control board which allows the nozzles to be activated separately, or in combination as required.

A "simulation set" consists of turning on the first nozzle closest to the collection flume, and running the equivalent of a small plot scale simulation. After a preset length of time (usually 20 minutes), which is long enough for the runoff rate to reach steady state, the second nozzle is turned on and the simulation procedure repeated. This "scale up" of plot size is repeated for all size nozzles until the entire plot is being rained on. After the runoff rate for the six nozzle simulation reaches a steady state, the sequence is reversed with each of the nozzles being systematically shut off, and the steady state runoff, measured. Runoff rate and sediment loss from each spatial scale are collected along with detailed measurements of soil water content along the length of the plot from 25 installed Time Domain Reflectrometry TDR soil probes.

The sediment samples for all of the simulation runs are analysed for phosphorus, particle size distribution, and ^{137}Cs. The source soil from the runoff plots are also analysed for the same properties and sediment enrichment ratios are calculated.

At each of the runoff sites detailed measurements of surface roughness are being made in addition extensive measurements of the soil hydraulic properties are being made. These measurements were augmented by SWEEP-TED contract to test the new Guelph surface permeameter at the same runoff sites.

Results from the study indicated that no-till systems usually had higher runoff rates (lower infiltration) than the moldboard tillage system. However, the total soil loss and phosphorus loss from the moldboard treatment were higher. The runoff data is consistent with measurements of the hydraulic properties. The soil bulk density increased in the no-till with a subsequent decrease in total porosity. The decrease in total porosity was in macro-porosity which would account for the decreased infiltration. Measurements of saturated hydraulic conductivity and field saturated hydraulic conductivity were also significantly lower in the no-till system. The soil matrix flux potential was lower in the no-till system which along with higher initial soil water contents resulted in shorter predicted and measured time to ponding.

Scale Linkage

The similarity in the measured effects of tillage on the hydraulic and physical properties of the soil, and the measured relative differences in the runoff characteristics was encouraging. It suggested that relative runoff characteristics can be estimated from soil properties. However, a fundamental problem exists in trying to estimate absolute values of runoff characteristics. This problem is related to the problem of scale linkages and the fact that the hydraulic properties within landscapes are not single values, but rather a distribution of values with a specific probability distribution function.

a) Spatial Scale

The data indicated that the measurement of steady infiltration rate changed (increased) as the scale of the plot increased. the amount of change (scale dependance) was larger for the moldboard tillage system. The minimum plot size to encompass all of the infiltration variability (and thus obtain a scale independent value) will depend on the soil variability at the site, and the influence of the tillage system on the soil variability. The spatial variability of the hydraulic properties was usually significantly higher in the MB treatment. Thus, it is not surprising that the moldboard treatment was more sensitive to scaling.

(b) Rainfall intensity

The previous annual report mentioned the problem that changing the rainfall intensity changed the steady-state infiltration rate. At one site, as the rainfall rates changed from 4.1 cm/hour (low) to 16.8 cm/hour the measured steady state infiltration rate increased from 3.4 to 7.0 cm/hour. The effect of rainfall intensity can be explained by the variability of the soil hydraulic properties. For example, a soil with an average saturated hydraulic conductivity k_{sat} of 4.0 cm/hour should have an average steady-state infiltration rate of 4.0 cm/hour. However, if the rainfall rate were 4.0 cm/hour you would still get runoff because the 4.0 cm/hour infiltration rate is an average infiltration rate, and at least 1/2 of the plot must have a lower infiltration rate and would generate runoff. some of this runoff water will make it to end of the plot and be measured as runoff. Thus, the steady measured infiltration rate will be somewhat lower than 4.0 cm/hour. If you apply water at a higher rate the infiltration rate will increase because at least 1/2 of the area has a higher infiltration rate. Only when the entire area has been ponded will the infiltration rate become constant.

The use of physically based models to predict soil loss and surface runoff assume that smaller scale heterogeneity can be lumped into effective parameter values. The data from this study support recent theoretical studies suggesting it may be difficult to define effective hydrologic variables that will adequately represent the behaviour of a heterogeneous hillslope. If this is true, then physical models based on effective (average) hillslope properties have limited practical predictive value. Stochastic methods of linking observation at different scales are being examined.

BP12

VALIDATION OF SPOTTAIL SHINER DAILY OTOLITH RINGS

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INTRODUCTION

This document reports to the Ontario Ministry of Environment our study on the ageing of spottail shiner (*Notropis hudsonius*). Although the grant's terms were addressed towards the spottail shiner, our attempts to collect that species met with little success in the early summer. However, we did capture on almost every occasion, the more common, bluntnose minnow (*P. notatus*). Since both species do overlap in their distribution, and are of comparable size in their first summer, we decided to include a comparison of age and growth for both species. The bluntnose minnow, however, appears to be a multiple (fractional) spawner, whereas the spottail does not, at least in our study site, 12-mile Lake.

The spottail shiner is used as a biomonitor of contaminants for the Great Lakes area, the body burden of metals and pollutants having been analyzed over a number of years by Karl Suns and his colleagues. To make the interpretation more accurate and more meaningful, Suns suggested that a knowledge of the precise ages of spottail (in relation to their size) would be most useful. Our intent was therefore, in this preliminary study, to assess the best method of ageing for DGIs (daily growth increments), and to validate the age and growth over the first summer from one study site. An accurate assessment of the size of "young-of-year" as opposed to 1+ fish was our first goal.

Only one other study has been carried out on the DGIs of cyprinidae, that of Victor and Brothers (1). They validated the age and growth of the fallfish (*Semotilus corporalis*), using the lapillus otolith (one of the 3 pairs of earbones found in bony fish.) Under a magnification of 400 - 1000x, this otolith clearly showed checks, yearly annuli, and DGIs. Because we obtained only a few eggs of spottail and reared them to validate the ages in days, we chose to follow length modes over time, and to inject fish with tetracycline to make a "mark" on the earbone as a reference point.

METHODS

A series of spottail shiners was collected randomly by seine from the same area in 12-mile Lake, Minden Co. These fish were preserved in 70% alcohol, measured, and the otoliths removed. A series of bluntnose minnows was also collected from Rice and Scugog lakes, and treated in the same way. Otoliths were mounted on slides, and viewed under 400x and 1000x with oil. The otoliths of fish over 4 cm in length required grinding, to elucidate the DGIs. Otherwise they were too thick to read accurately.

Modes in the length of fish and back calculations of the age in days were matched to the mean sizes in length. This method was successful for spottail, but since bluntnose is a fractional spawner, modes were less distinct. The otoliths of these two closely related species were very similar, although those of the spottail were rounder and the rings were more closely spaced than those of the bluntnose minnow.

RESULTS

For spottail, the changes in length modes over time showed that rings were laid down in a daily pattern. The back-calculated ages led to a hatch date of mid-May. Although spawning dates are not well documented, it is close to the observed date of spawning in Lake Simco (Ross, personal comm.) spawners, as opposed to the spottail, which spawn only once in 12-mile Lake (although this is possible they may spawn more frequently in their more southerly range.

In mid-July, most Y.O.Y.s ranged in length from 24-37 mm TL, and averaged 60 DGIs. By back calculation, hatch date was about mid-May. By August, average size was 36-54 mm TL, with ages corresponding to hatches of May 23, and May 29 (Table 1A). Within this size range there were also some yearlings in the catches.

Bluntnose minnows showed equally clear microzones, and back calculations suggested a May 15-20 for first hatch date period. (Table 2A) .

Figure 1A shows clearly the sizes of Y.O.Y. and 1+ bluntnose minnows were separated into modes in their length frequencies for mid-June to 22 July. By September, there was a wide range in the length frequency distribution, not so easily separable by modal peaks. On the basis of these modes and the growth curve, (not shown), the fish showed a logical sequence of increase in length in relation to days. The growth rates of both spottail and bluntnosed were quite similar.

By the end of the first summer, spottail in 12-mile achieved a length of 42 mm TL for young-of-year and over 50 mm TL for 1+, while available samples from southern Ontario for 1+ fish reached 6-7 cm TL. The smallest 1+ observed in July was 42 mm TL and by August, 60 mm. Thus, there is overlap. A preliminary key to the lengths of young-of-year fish of both species estimated from these data is shown below.

Table 1A. Spottail shiners ages in days (DGIs) for various dates, 12-mile Lake. 1988.

Sampling Date	DGIs (Average No.)	Mean TL	Hatch estimate
14 July 1988	53	24 mm	May 22
22 July 1988	58	30 mm	May 24
03 August 1988	70	32 mm	May 23
17 August 1988	76	42 mm	May 29

Table 1B. Y.O.Y. Age length key - Spottail shiner

Date of Capture	Kawarthas	Southern Ontario
Mid-July	under 4.0 cm TL	under 4.5 cm TL
3rd wk July	" 4.5 " "	" 5.0 " "
1st wk August	" 5.0 " "	" 6.0 " "
Mid-August	" 5.4 " "	" 6.5 " "

Table 2A Bluntnose Minnow Kawarthas Hatch Dates (approx) derived from DGIs.

Sampling Date	Average No. DGIs	Hatch Date
27 June 1988	45	May 15
22 July 1988	57	May 20

Table 2B Bluntnose minnow Y.O.Y. age length key, Kawarthas

End of June	Rice Lake	5.0 cm TL
End of July	Rice/Scugog	4.4 cm TL
End August	Rice	5.5 cm TL

DISCUSSION

There remain two aspects of the ageing biology of spottail shiner to be investigated prior to our complete satisfaction of the accuracy of the technique. There appeared to be subdaily rings on the otoliths of some fish, which resulted in a hatch date (after back calculation) which was unreasonably early. Injections of tetracycline and holding experiments are needed to solve this physiological question. Of seven small fish (8-11 mm TL) reared by Karl Suns from the eggs, and maintained for one month, the ages ranged from 35-40, which suggests excess daily rings in the early stages of growth. This confirmed our suspicion of the above. Secondly, a method should be developed to mark the annulus of otoliths so that they can be compared to the assumed annulus on the scales, which are far less tedious to read than otolith daily rings, but are more subject to "false annulus" formation.

ACKNOWLEDGEMENTS

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(This is the only age study published on a freshwater cyprinid, using daily growth increments and relating the study to yearly annuli).

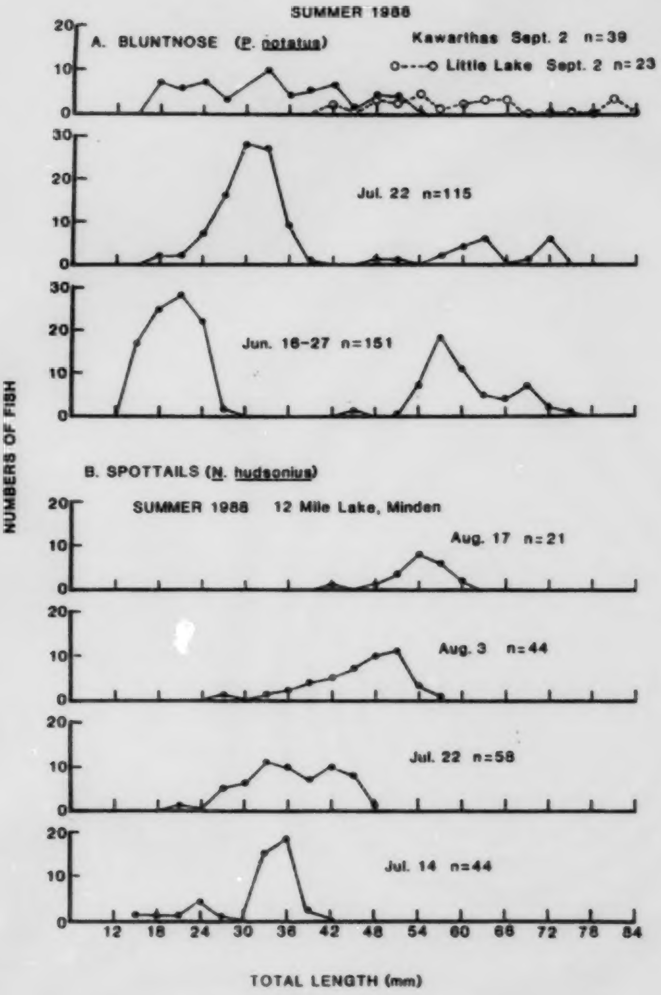

Fig. 1: Length of frequency distributions of bluntnose minnow and spottail shiner, 1988, taken by small-mesh beach seine.

BP13

An Investigation of the Potential of Zygnematacean Zygospores, Peridinium, and Pediastrum as Paleo-indicators of Recent Lake Acidification.

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The increased growth of certain Zygnematacean algae in softwater lakes during the early stages of lake acidification has prompted an investigation of the potential use of zygospores of this family as paleoindicators of early acidification. The main purpose of the investigation was not to replace the transfer functions developed for diatoms and other siliceous scale-bearing Chrysophyceae, but rather to provide a more complete overview of past lake dynamics, especially in lakes where a clear relationship between diatoms, Chrysophyceae and pH cannot readily be established. Certain species of the filamentous green Zygnemataceae increase in abundance as pH drops to about 6.0. Zygospores have been described and in many cases can be used to characterize the species.

In the Fall of 1989, sediment cores were taken from 11 lakes in the Haliburton-Muskoka region of Ontario. To date, most of our effort has been directed to standardizing and testing techniques for the recovery and concentration of Zygnematacean zygospores from lake sediments. These zygospores are made of a sporopollenin-like substance, which is composed of oxidative polymers of carotenoids or carotenoid esters. The material is very resistant to decay and persists for millions of years in sediments.

The presentation will describe the steps developed for sample splitting, addition of marker grains, removal of carbonate, iron-oxy-hydroxide, and silicate minerals and fluoride by-products, removal of humic material and the removal of cellulose and hemicellulose by acetolysis. The flow chart below illustrates the steps for concentrating sporopollenin cysts from typical lake sediments.

1. Measure de-watered sediment volume
   2-3 ml of raw sediment exclusive of large vegetative or mineral fragments
   centrifuge at high speed to de-water sediment
   add known quantity of Lycopodium tablets - yields density: specimens/ml.
   Examine bulk sediment describe mineral and organic component.

2. Carbonate Removal - HCl
   removes calcareous algae, limestone and dolomite; dissolves tablets containing marker grains.

3. Humic acid removal - NH_4OH
   disperses organic floccules and removes humic material, oxidized cellulose, clay- sized amorphous mineral and organic particles.
   Examine general relationships between all fossil groups (except calcareous algae).
   Sample cut for diatom analysis.

4. Silica and silicate removal - HF
   removes diatoms, sponge spicules, and silicate minerals.
   Examine cellulosic remains, many types of algae preserved.
   Sample cut and slides made for algal analysis.

5. Acetolysis — H_2SO_4 : $(CH_3CO)_2O$ (1:9)
removes cellulose and hemi-cellulose.
Make final slides for analysis.
Only "sporopollenin" remains;
spores, pollen, dinoflagellates, pediastrum, and
zygospores.

Zygnematacean zygospores are more resistant to oxidizing acids than most types of pollen. Further concentration of Zygnematacean zygospores from the overwhelmingly abundant pollen may be possible by controlled oxidation of the residue. Attempts at concentrating Zygnematacean zygospores by oxidation with chromic acid and nitric acid have both show promising results, but has not resulted in a practical method for yield a statistically reliable concentration of zygospores.

Preliminary results suggest that while the frequency of Zygnematacean zygospores may limit their usefulness as paleoindicators of acidification, nevertheless, other algal cysts formed of sporopollenin, especially *Pediastrum* spp. and *Peridinium* spp. may be more useful, since they exhibit clear pH preferences over the range of interest, and are more abundant than the Zygnematacean spores in the samples which have been studied to date.

Over 40 types of acid-base-acetolysis resistant (mostly algal) cysts were encountered in the organic residues that were concentrated from the lake sediments. Table 1 illustrates reconnaissance level results for the abundance of cysts of the dinoflagellate genus *Peridinium* and coenobia of *Pediastrum*. Cysts of *Peridinium* can readily be identified to species level for at least 4 species. Coenobia of *Pediastrum* can be identified to species and often varietal level. A general relationship of higher diversity of *Peridinium* cysts and lower diversity of *Pediastrum* coenobia to decreasing pH values is apparent in Table 1. Cysts of *Peridinium limbatum* and *P. wisconsinense* are associated with lower pH lakes, while common occurrences of most species and varieties of *Pediastrum* occur in lakes with higher pH. Ongoing quantitative analysis will show if a successful paleo-indicator of pH may be derived by using a combination of diversity measures and pH-related species entry levels for *Peridinium*, *Pediastrum* and several types of green algae with cell walls formed of sporopollenin.

Lake	pH	Microflora recovered from surface sediments ——>													
		Peridinium				*Pediastrum*									
		limb	wisc	bipes	willeii	araR	bory	borL	borS	dupl	dupC	inte	intP	intS	Zygs
Leonard	5.5	A	A	C	P	P									
Plastic	5.7	AA	C	C	C										P
Tock	6.4	C	C	C	P	C		P							?
St. Nora	6.6	C	C	C	P										?
Rabbit Bay	6.7		P	P	C										
Kushog	6.8			P	C	C	P								
Harp	6.8				C							C			P
Little Clear	6.9			C	C	C	C					P	P		
4 Mile	7.8			C	C		C		C	C					P
White	8.7				P		C				C	C		C	

Table 1 - Reconaissance tabulation of algal cysts recovered from surface samples from 10 lakes in the Haliburton—Muskoka region of Ontario during the Fall of 1989.

Legend for Table 1:

Peridinium
limb= P. limbatum
wisc.= P. wisconsinense
bipes= P. bipes
willeii= P. willeii

Pediastrum
araR= P. araneosum rugulosum
bory= P. boryanum
boryL= P. boryanum longicorne
boryS= P. boryanum (smooth)
dupl= P. duplex
dupC= P. duplex clathratum
inte= P. integrum
inteP= P. integrum priva
inteS= P. integrum scutum

Zygnemataceae
zygs= smooth wall ellipsoidal zygo-spores unidentifiable at genus level.

AA= very abundant
A= abundant
C= common
P= present

Core samples from Plastic lake are currently being analyzed for *Peridinium* cysts, *Pediastrum* coenobia and other types of sporopollenin based algae cysts. Paleo-environmental interpretations will be made from relationships determined from the analysis of surface samples from lakes listed in Table 1.

Volume

2

ENVIRONMENTAL RESEARCH

TECHNOLOGY TRANSFER CONFERENCE · CONGRES SUR LE TRANSFERT DES TECHNIQUES

LES RECHERCHES SUR L'ENVIRONNEMENT

ISSN 0825-4591

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VOLUME II:

KEYNOTE PRESENTATIONS
FEATURE PRESENTATIONS
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ANALYTICAL METHODS RESEARCH
ENVIRONMENTAL SOCIO-ECONOMICS RESEARCH
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THE CHALLENGES OF A NEW DECADE

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Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1990 Technology Transfer Conference are published in two volumes of conference Proceedings corresponding to the following sessions:

VOLUME I: KEYNOTE PRESENTATIONS
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WATER QUALITY RESEARCH

VOLUME II: KEYNOTE PRESENTATIONS
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LIQUID & SOLID WASTE RESEARCH
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Volume II is comprised of presentations given during Session C, Session D, Session E and Session C of the conference, as well as all Keynote, Feature, and Panel Presentations.

For reference purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573

Acknowledgments

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

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VOLUME I

INDEX

Keynote Presenters

Page

Sustainable Development: The Technological Challenge; Noel J. Brown, Director, United Nations Environment Programme 1

Responses to Global Climate Change: The Coming Environmental and Economic Revolutions; Jim Bruce, Chair, Canadian Climate Program Board 2

Feature Presenters

Air Quality Research

A1 **What's the Latest on Acidic Deposition in North America?;** D. Sisterson, Argonne National Laboratory, Argonne, Illinois, USA 5

A10 **Measurement of Semi-Volatile Organic Compounds in Ambient Air;** G. Hunt, ENSR, Acton, Massachusetts, USA 7

Water Quality Research

B1 **Influence of the Zebra Mussel *(Dreissena polymorpha)* on Water Quality of Lake Erie;** J. Leach, Ontario Ministry of Natural Resources, Wheatley, Ontario 8

B10 **Cross-Disciplinary Analyses of Environmental Health Studies Suggest the Need for New Approaches to Risk Assessment;** T. Colborn, US Conservation Foundation, Washington D.C., USA 10

Volume I **Page**

Liquid & Solid Waste Research

C1 **Environmental Concerns - Keeping our Perspective;** J.P. Nunan, Trow, Dames & Moore, Mississauga, Ontario 12

C10 **Oxidation to Remove Trichloroethylene from Soil;** G. Farquhar, University of Waterloo, Waterloo, Ontario 16

Analytical Methods Research

D1 **Ion Mobility Spectrometry in Atmospheric Environmental Monitoring in the U.S. Space Program;** G.A. Eiceman, New Mexico State University, Las Cruces, New Mexico 17

Environmental Socio-Economics

E1 **Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market;** B. Hull, The Conference Board of Canada, Ottawa, Ontario 19

Multimedia Contaminants & Biotechnology

F1 **Utilization of Environmental Research to Control Lead Contamination;** B.G. Wixson, Clemson University, Clemson, South Carolina, USA 20

Panel Presentations

Global Warming: What is at Stake?

P1 **The International Scene;** J.P. Bruce, Chair, Canadian Climate Program Board 26

P2 **Global Warming: A Canadian Perspective and Action Strategy;** D.K. Dawson, Director General, Canadian Climate Centre 27

Volume I Page

P3 **Global Warming: What is at Stake? Socio-Economics;** E. Haites, Barakat & Chamberlin Inc. 28

P4 **Warming to a Crisis: The Media and Climate Change;** M. Keating, Environmental Writer 32

P5 J.D. McFarland, Imperial Oil Limited 36

P6 **Global Warming: What's Known and What's Not?;** B. Yang, Ontario Cabinet Office 37

VOLUME I

SESSION A: AIR QUALITY RESEARCH

Verbal Presentations

		Page
A2	**Genetic Characteristics of Healthy and Declining Sugar Maple *(Acer saccharum Marsh)* in Ontario;** P. Knowles, Lakehead University, Thunder Bay, Ontario	38
A3	**Interpretation of Sugar Maple *(Acer saccharum)* Ring Chronologies from Central and Southern Ontario using a Mixed Linear Model;** D.A.J. Ryan*, O.B. Allen and A.M. Gordon, University of Guelph, Guelph, Ontario	46
A4	**A Method to Establish Background Concentrations of Contaminants and Nutrients in Soil and Vegetation;** R. Jones, Air Resources Branch, Environment Ontario, Toronto, Ontario	53
A5	**Further Developments in the Analysis of Three Dimensional Environmental Data;** P.K. Hopke* and Y. Zeng, Clarkson University, Potsdam, New York, USA	67
A6	**Evaluating the Comprehensive Model ADOM;** C. Fung*, R. Bloxam, P.K. Misra and S. Wong, Air Resources Branch, Environment Ontario, Toronto, Ontario	80
A7	**Modeling the Influence of Topography on Dense Gas Dispersion;** S.R. Ramsay* and R.E. Britter, EnviroTech Research Limited, London, Ontario	88

Volume I **Page**

A8 **Ignition Studies of Selected Explosive Mixtures of Gases and Dusts Emitted from Cement Kilns;** I.I. Inculet*, E.J. Weckman, G.S.P. Castle, K.A. Shelstad and M.L. Wick, The University of Western Ontario, London, Ontario 99

A9 **Evaluation of Methods to Determine the Impacts of Residential Woodburning on Ambient Air in Ontario;** M.E. Yandle*, C.S. Davis and D.L.M. Dougherty, Concord Scientific Corporation, Downsview, Ontario 104

A11 **A Study of the Peak Ozone Levels in the Toronto Area;** J.D. Smith* and L. Shenfeld, The MEP Co., Markham, Ontario 118

A12 **Developments of Monitoring Methods for Odorous Organics in Ambient Air;** C. Chan*, P. Forsythe, L. Vainer and J.W. Martin, Mann Testing Laboratories, Mississauga, Ontario 128

A13 **Atmospheric Measurements of Natural Hydrocarbons Using Gas Chromatography/Mass Spectrometry;** H. Niki* and B.H. Khouw, York University, North York, Ontario 136

A14 **Atmospheric Trace Gas Measurements Using a Tunable Diode Laser Absorption Spectrometer;** H.I. Schiff*, R. Berman, D.R. Hastie and S. Sharma, York University, North York, Ontario 149

Volume I **Page**

A15 **Uptake and Distribution of Naphthalene in Vegetable Plants Following Foliar and Root Exposure;** B. Hale-Marie* and D.P. Ormrod, University of Guelph, Guelph, Ontario 157

A16 **Phytotoxicity of Uranium;** S.C. Sheppard*, W.G. Evenden and A.J. Anderson, AECL Research, Pinawa, Manitoba 165

VOLUME I

SESSION A: AIR QUALITY RESEARCH

Poster Presentations **Page**

AP1 **Identification of Odours. The Challenge of the Nineties;** A.C. Ng and G.B. De Brou, Air Resources Branch, Environment Ontario, Toronto, Ontario 173

AP2 **CO_2 Production and Carbon Cycling in Precambrian Shield Watersheds;** R. Aravena and S.L. Schiff, University of Waterloo, Waterloo, Ontario 177

AP3 **Modelling the Long Range Transport, Transformation and Deposition of Mercury;** R. Bloxam, S. Wong and P.K. Misra, Air Resources Branch, Environment Ontario, Rexdale, Ontario, E. Voldner and W. Schroeder, Atmospheric Environment Service, Environment Canada, G. Petersen, GKSS Research Centre, Germany 181

AP4 **An Investigation of Vibration Isolation in a House for Reduction of Train Vibration;** G. Pernica and J.H. Rainer, National Research Council Canada, Ottawa, Ontario 189

AP5 **Simultaneous Real Time Detection of Mercury and Hydrogen Chloride in Ambient Air;** M.D. Corbridge, G.B. DeBrou, A. Ng and N.S. Karellas, Air Resources Branch, Environment Ontario, Toronto, Ontario 192

Volume I **Page**

AP6 **A Residence Time Analysis of Air Data from the Acidic Precipitation in Ontario Study (APIOS);** N.W. Reid, A.J.S. Tang, M. Lusis and D. Yap, Air Resources Branch, Environment Ontario, Toronto, Ontario **196**

AP7 **Microwave Induced Catalytic Decomposition of Some Gaseous Air Pollutants;** M.C. Depew, T. Dineson, M.Y. Tse and J.K.S. Wan, Queen's University, Kingston, Ontario **200**

AP8 **Mesoscale and Long Range Transport Models are Combined to Model Pollutants Originating from Local and Distant Sources;** M. Niewiadomski, The MEP Company, Markham, Ontario **206**

AP9 **Relationship of Suger Maple Decline and Corresponding Chemical Changes in Sap Carbohydrates and Trace Elements;** D.N. Roy, S. Pathak, H.K. Mohamed and T.C. Hutchinson, University of Toronto, Toronto, Ontario **210**

AP10 **Modelling Concentration Fluctuations;** E. Alp and A. Ciccone, Concord Scientific Corporation, Downsview, Ontario and C.S. Fung, Environment Ontario, Toronto, Ontario **214**

VOLUME I

SESSION B: WATER QUALITY RESEARCH

Verbal Presentations

		Page
B2	**Early Biological and Life History Attributes of the Zebra Mussel, *Dreissena polymorpha* (Bivalvia: Dreissenidae), and Impacts on Native Bivalves in Lake St. Clair;** G.L. Mackie, University of Guelph, Guelph, Ontario	215
B3	**Toxicokinetic Modelling of Mixtures of Organic Chemicals;** L.S. McCarty*, G.W. Ozburn and A.D. Smith, Lakehead University, Thunder Bay, Ontario and D.G. Dixon, University of Waterloo, Waterloo, Ontario	232
B4	**Verification of a Bioconcentration-Based Model for Predicting Pulse-Exposure Toxicity of Organic Contaminants to Fish;** B.E. Hickie* and D.G. Dixon, University of Waterloo, Waterloo, Ontario	242
B5	**Mapping Lake Water Quality Characteristics Using Landsat Thematic Mapper Data;** J.R. Pitblado*, T.L.M. Jetty, R.L. O'Daiskey and D.A. Dempsey, Laurentian University, Sudbury, Ontario	250
B6	**Multispectral Remote Sensing Techniques for Past, Present and Future Mapping of Chlorophyll;** A.R. Kalinauskas*, Moniteq Ltd, Concord, Ontario, N.J. Hutchinson and B.P. Neary, Dorset Research Centre, Environment Ontario, Dorset, Ontario	256

Volume I		Page
B7	**Regional Analysis of Low Flow Characteristics for Central and Southeastern Regions;** H.S. Belore*, D.A. Ashfield and S.P. Singh, Cumming Cockburn Limited, Willowdale, Ontario	258
B8	**Retractable Composite Absorbents for Environmental Clean-Up;** B. Gillies* and H. Auksi, Eco Corporation, Willowdale, Ontario and O. Meresz, Laboratory Services Branch, Environment Ontario, Toronto, Ontario	270
B9	**Advanced Technology for Destruction of Organic Pollutants in Water Streams;** H. Al-Ekabi*, A. Safarzadeh-Amiri, J. Story, W. Holden and G. Edwards, Nulite, a Division of Nutech Energy Systems Inc., London, Ontario	275
B11	**Carcinogenicity Testing of Bleached Kraft Mill Effluent Using *In-vivo* Rainbow Trout Assays;** C.D. Metcalfe*, M.E. Nanni and N.M. Scully, Trent University, Peterborough, Ontario	287
B12	**Impact of Bleached Kraft Mill Effluent (BKME) on Fish Populations Near Terrace Bay, Ontario;** M.E. McMaster* and D.G. Dixon, University of Waterloo, K.R. Munkittrick, Great Lakes Fisheries, C. Portt, C. Portt and Associates, G.J. Van der Kraak, University of Guelph, I.R. Smith and D. Rokosh, Environment Ontario	295

Volume I Page

B13 **Involvement of Bile Duct Disease and Loss of Resistance to Chemical Carcinogens in the Pathogenesis of Liver Neoplasms in Benthic Fish from Lake Ontario;** G.M. Kirby*, P. Byrne, M.J. Stalker, I.R. Smith and M.A. Hayes, University of Guelph, Guelph, Ontario 302

B14 **The Use of Benthic Invertebrates in Mapping Toxic Areas of Sediment and Determining the Efficacy of Sediment Cleanup Operations;** M. Dickman*, F. Fiore and I. Brindle, Brock University, St. Catharines, Ontario 317

B15 **Monitoring of Organic Contaminants in Aquatic Food-Chains;** G.D. Haffner*, F.A.P.C. Gobas, R. Lazar and D. Laviolet, University of Windsor, Windsor, Ontario 327

B16 **PCB Dynamics of Pottersburg Creek, London, Ontario;** D.T. Zaranko*, K.R. Solomon and N.K. Kaushik, University of Guelph, Guelph, Ontario 328

VOLUME I

SESSION B: WATER QUALITY RESEARCH

Poster Presentations		Page
BP1	**Development of an Improved System for the Application of Powdered Activated Carbon in Potable Water Treatment;** H.E. Donison and A. Benedek, ZENON Environmental Inc., Burlington, Ontario	340
BP2	**Geochemical Associations of Cd, Cu, Pb and Zn with Suspended Particulates in the Don River;** L.A. Warren and A.P. Zimmerman, University of Toronto, Toronto, Ontario	343
BP3	**The Effects of Agricultural Drainage on Sediment and Water Quality Loadings;** J.D. Paine, W.E. Watt and S.A. Peters, Queen's University, Kingston, Ontario	344
BP4	**Chronic Effects of Thiocyanate on Freshwater Fish: Development of a Water Criterion;** R.P. Lanno and D.G. Dixon, University of Waterloo, Waterloo, Ontario	349
BP5	**Zooplankton Communities and Water Chemistry of Sudbury Area Lakes: Changes Related to pH Recovery;** A. Locke and W.G. Sprules, University of Toronto, Mississauga, Ontario	358
BP6	**The Relative Effect of Individual Environmental Factors on Indicator Bacterial Survival;** E. Harris, Lake Simcoe Region Conservation Authority, Newmarket, Ontario	359

Volume I

Page

BP7 **The Effect of Farm Liquid Waste Application on Receiving Water Quality;** D.M. Dean and M.E. Foran, Ausable Bayfield Conservation Authority, Exeter, Ontario 365

BP8 **Statistical Assessment of Multivariate Ordination Techniques for Zoobenthic Communities and Water Chemistry for Lakes from Central Ontario;** D.A. Jackson and H.H. Harvey, University of Toronto, Toronto, Ontario 370

BP9 **Geochemical Alteration of Road De-Icing Chemicals by Sub-Surface Rock-Soil-Water Interactions;** K.W.F. Howard and J. Haynes, University of Toronto, Scarborough, Ontario 371

BP10 **Standardized Rearing Materials and Procedures for *Hexagenia*, a Benthic Bioassay Organism: Comparison of Sediment Types;** E.C. Hanes, J.J.H. Ciborowski and L.D. Corkum, University of Windsor, Windsor, Ontario 374

BP11 **Tillage and Event Based Soil and Water Loss: Scale Linkages;** R.G. Kachanoski, W.T. Dickinson and R. Rudra, University of Guelph, Guelph, Ontario and University of Waterloo, Waterloo, Ontario 383

BP12 **Validation of Spottail Shiner Daily Otolith Rings;** P.M. Powles, B.A. Powles and R.A. Curry, Trent University, Peterborough, Ontario 386

BP13 **An Investigation of the Potential of Zygnematacean Zygospores, Peridinium, and Pediastrum as Paleo-Indicators of Recent Lake Acidification;** P. Zippi, Y-K Yung, J.A. McAndrews, G. Norris and P. Welbourn, University of Toronto, Toronto, Ontario 393

VOLUME II

INDEX

Keynote Presenters

Page

Sustainable Development: The Technological Challenge; Noel J. Brown, Director, United Nations Environment Programme 397

Responses to Global Climate Change: The Coming Environmental and Economic Revolutions; Jim Bruce, Chair, Canadian Climate Program Board 398

Feature Presenters

Air Quality Research

A1 **What's the Latest on Acidic Deposition in North America?;** D. Sisterson, Argonne National Laboratory, Argonne, Illinois, USA 401

A10 **Measurement of Semi-Volatile Organic Compounds in Ambient Air;** G. Hunt, ENSR, Acton, Massachusetts, USA 403

Water Quality Research

B1 **Influence of the Zebra Mussel *(Dreissena polymorpha)* on Water Quality of Lake Erie;** J. Leach, Ontario Ministry of Natural Resources, Wheatley, Ontario 404

B10 **Cross-Disciplinary Analyses of Environmental Health Studies Suggest the Need for New Approaches to Risk Assessment;** T. Colborn, US Conservation Foundation, Washington D.C., USA 406

Volume II **Page**

Liquid & Solid Waste Research

C1 **Environmental Concerns - Keeping our Perspective;** J.P. Nunan, Trow, Dames & Moore, Mississauga, Ontario 408

C10 **Oxidation to Remove Trichloroethylene from Soil;** G. Farquhar, University of Waterloo, Waterloo, Ontario 412

Analytical Methods Research

D1 **Ion Mobility Spectrometry in Atmospheric Environmental Monitoring in the U.S. Space Program;** G.A. Eiceman, New Mexico State University, Las Cruces, New Mexico 413

Environmental Socio-Economics

E1 **Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market;** B. Hull, The Conference Board of Canada, Ottawa, Ontario 415

Multimedia Contaminants & Biotechnology

F1 **Utilization of Environmental Research to Control Lead Contamination;** B.G. Wixson, Clemson University, Clemson, South Carolina, USA 416

Panel Presentations

Global Warming: What is at Stake?

P1 **The International Scene;** J.P. Bruce, Chair, Canadian Climate Program Board 422

P2 **Global Warming: A Canadian Perspective and Action Strategy;** D.K. Dawson, Director General, Canadian Climate Centre 423

Volume II Page

P3 **Global Warming: What is at Stake? Socio-Economics**; E. Haites, Barakat & Chamberlin Inc. 424

P4 **Warming to a Crisis: The Media and Climate Change**; M. Keating, Environmental Writer 428

P5 J.D. McFarland, Imperial Oil Limited 432

P6 **Global Warming: What's Known and What's Not?**; B. Yang, Ontario Cabinet Office 433

VOLUME II

SESSION C: LIQUID & SOLID WASTE RESEARCH

Verbal Presentations **Page**

C2 **Manual for Establishing Vegetation on Erosion-Prone Landfill Slopes in Ontario;** N. DeFraeye* and T.W. Hilditch, Gartner Lee Limited, Markham, Ontario 434

C3 **Quantification of Infiltration Through Landfill Covers;** K.J. McKague*, Ecologistics Limited, Waterloo, Ontario and J.H. Cuthill, University of Guelph, Guelph, Ontario 442

C4 **Accurate Control Testing for Clay Liner Permeability;** R.J. Mitchell, Queen's University, Kingston, Ontario 456

C5 **Field Demonstration of Membrane Technology for Treatment of Landfill Leachate;** C.M. Smith* and T.A. Krug, Zenon Environmental Inc., Burlington, Ontario 464

C6 **Slow Rate Infiltration Land Treatment and Recirculation of MSW Landfill Leachate in Ontario;** R.A. McBride*, A.M. Gordon, P.H. Groenevelt, T.J. Gillespie and L.J. Evans, University of Guelph, Guelph, Ontario 475

C7 **Determination of Hydro-geological and Contamination Transport Properties of Fractured Weathered Leda Clay in Eastern Ontario;** A.Y. D'Astous*, Envir-Eau Inc., Hull, Quebec and N.G. Castonguay, Fondex Ltd., Nepean, Ontario 485

Volume II Page

C8 **The Characterization of Two Discrete Horizontal Fractures in Shale;** P.A. Lapcevic* and K.S. Novakowski, National Water Research Institute, Burlington, Ontario and J.A. Cherry, University of Waterloo, Waterloo, Ontario 486

C9 **The Origin and Distribution of Methane in the Alliston Sand Aquifer Complex;** R. Aravena*, L. Wassenaar, J. Barker and R.W. Gillham, University of Waterloo, Waterloo, Ontario 496

C11 **The Recycling of Steelmaking Dusts Using the LB Furnace;** Q.S. He, C. Bryk and W.K. Lu*, McMaster University, Hamilton, Ontario 505

C12 ***In Situ* Biodegradation of Chlorinated Solvents;** D.W. Major* and E.W. Hodgins, Beak Consultants Limited, Guelph, Ontario 518

C13 **Glassification and Leachability of Hazardous Wastes and Hazardous Waste Residues;** K.B. Harvey, AECL Research, Whiteshell Laboratories, Pinawa, Manitoba 519

C14 **Non-Linear Sorption of Phenol on Natural Clay and its Influence on Diffusive Migration;** J.P. Mucklow* and R.M. Quigley, The University of Western Ontario, London, Ontario 520

C15 **Estimating Landfill Leachate and Contaminant Production;** L. Jarvis* and G. Farquhar, University of Waterloo, Waterloo, Ontario 530

C16 **Test of a Chemical Mechanical Process for the Decontamination of Non-Anatomical Biomedical Waste;** P.L. Seyfried*, T. Bleier, S. Qaiyumi, B.-L. Xu, N. Anderson, C.C. Tse, and N. Azami, University of Toronto, Toronto, Ontario 540

VOLUME II

SESSION C: LIQUID & SOLID WASTE RESEARCH

Poster Presentations Page

CP1 **Purification and Detoxification of Textile Dyebath Effluent by Electrochemical Treatment;** A.E. Wilcock, University of Guelph, Guelph, Ontario 548

CP2 **Stabilization of a Waste in a Landfill Environment;** M. Modi and D.W. Kirk, University of Toronto, Toronto, Ontario 553

VOLUME II

SESSION D: ANALYTICAL METHODS RESEARCH

Verbal Presentations — Page

D2 **Coupling an External Source to a Fourier Transform Ion Cyclotron Resonance Spectrometer to Improve its Use for Analytical Purposes;** T.B. McMahon* and C.E.C.A. Hop, University of Waterloo, Waterloo, Ontario — 557

D3 **The Analysis of N-Nitrosodimethylamine in Environmental Samples by GC-MS;** J.-P. Palmentier*, V. Taguchi, E.J. Reiner, S.W.D. Jenkins, D.T. Wang, D. Robinson, R.J. Kleins and K.-P. Ngo, Environment Ontario, Rexdale, Ontario — 558

D4 **Real Time Measurements of Dimethylnitrosamine in Ambient Air by Mobile Tandem Mass Spectrometry;** N.S. Karellas*, G.B. DeBrou and A.C. Ng, Air Resources Branch, Environment Ontario, Toronto, Ontario — 561

D5 **The Analysis of Smithville Drinking Water for PCBs;** D. Sutherland*, J. Waugh, L. Paul, A. Rayner and G. Reuel, Canviro Ltd., Kitchener, Ontario — 569

D6 **Evaluation of Environmental Sources of Polychlorinated Biphenyls Using Chemometric Methods;** S. Davies*, Laboratory Services Branch, Environment Ontario, Toronto, Ontario and F. Onuska, Environment Canada, Burlington, Ontario — 574

Volume II **Page**

D7 **Isolation and Derivatization of Chloro-Aromatic Organic Acids on Solid Support;** J. Rosenfeld* and Y. Maharir, McMaster University, Hamilton, Ontario 584

D8 **Bias Due to Sampling Ground-Water and Surface Water for Trace Organic Contaminants;** J.T. Hoff*, C. Arthur, D. Baerg, J.F. Barker and R.W. Gilham, University of Waterloo, Waterloo, Ontario 592

D9 **Polynuclear Aromatic Hydrocarbons Identification Using GC/FT-IR and Pairs;** J. Semmler*, P. Yang and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 601

D10 **The Struggle Towards Virtual Elimination of Toxic Chemicals from the Environment;** D. MacKay, University of Toronto, Toronto, Ontario 615

D11 **Graphical Techniques for the Presentation of Inter-laboratory Study Data-A Diagnostic Aid;** S. Cussion* and D.E. King, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 618

D12 **Design, Constraints and Implementation of Rules Within ACexpert;** M.J. Stillman*, S. Lahiri and Q. Zhu, The University of Western Ontario, London, Ontario 628

D13 **An Apparatus for Rapid Microwave Sample Decomposition;** V. Karanassios*, F.H. Li and E.D. Salin, McGill University, Montreal, Quebec 640

Volume II Page

D14 **An Electrothermal Vaporization System for the Direct Analysis of Solids by ICP-AES;** E.D. Salin*, V. Karanassios and J. Ren, McGill University, Montreal, Quebec 648

D15 **Flow Injection Preconcentration/ Direct Sample Insertion for Trace Element Analysis by ICP-AES and ICP-MS;** P. Moss* and E.D. Salin, McGill University, Montreal, Quebec 655

D16 **Prereduction of Arsenic (V) to Arsenic (III), Enhancement of the Signal, and Reduction of Interferences by L-Cysteine in the Determination of Arsenic by Hydride Generation;** I.D. Brindle*, Brock University, St. Catharines, Ontario and H. Chen, Hangzhou University, Peoples Republic of China and X-C. Le, University of British Columbia, Vancouver, British Columbia 663

VOLUME II

SESSION D: ANALYTICAL METHODS RESEARCH

Poster Presentations **Page**

DP1 **Expert Systems in Analytical Chemistry. Design of a User Interface and Implementation of Rules for ACdiagnosis within ACexpert;** S. Lahiri, Q. Zhu and M.J. Stillman, University of Western Ontario, London, Ontario 672

DP2 **Development of a Turn-Key System for Hazardous Wastes Analysis;** P. Yang, M. Yang, J. Semmler and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 676

DP3 **Study of the Effect of Solvent and Stationary Phase on the Chromatographic Behavior of PAHs;** I.D. Brindle and X. Li, Brock University, St. Catharines, Ontario 688

DP4 **Monitoring Ambient Air VOCs Using Cryogenic and Adsorbent Trap: A Critical Evaluation;** P. Yang, L. Au, P. Ford, B. Foster and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 694

DP5 **Adaptation of Water Preconcentration Techniques Developed for PCDD Analysis to Other Target Organic Pollutants;** C. Shewchuk, L.J. Brownlee and B.R. Hollebone, Carleton University, Ottawa, Ontario 701

Volume II Page

DP6 **Complete Ambient Air VOCs and VOST POHCs Analyses Using One Single TD/GC/MS System;** L. Au, S. Kullar, P. Yang, P. Ford, B. Foster and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 707

DP7 **An Automated Gel Permeation Chromatographic Method for Cleanup of Sewage Sludge Extracts for GC/MS Analysis of Priority Organic Pollutants;** R. Lega, M. Meconnen, A. Salewski, G. Crawford, O. Meresz and I. Ahmad, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 716

DP8 **Simultaneous Derivatization – Extractions Technique for the Analysis of Acidic Organic Contaminants from Water – Feasibility Study with Diazomethane for the Analysis of 4-Amino – 3,5,6-Trichloro Picolinic Acid (Picloram);** R. Lega, O. Meresz and G. Crawford, Laboratory Services Branch, Environment Ontario, Rexdale, Ontario 722

DP9 **Brominated and Mixed Bromo/ Chloro Dibenzo-p-Dioxins and Dibenzofurans: Toxicological Properties, Analytical Methods and Occurrence;** B.G. Chittim and D.S. Waddell, Environmental Consultants Incorporated, Guelph, Ontario 727

Volume II **Page**

DP10 **Determination of Organolead Compounds in Indusirial Effluents;** M.J. Powell, I. Ahmad and L. Glassford, Environment Ontario, Rexdale, Ontario 730

DP11 **Techniques for Identification of Specific Sources of Airborne Particulates;** T. Lee, R. Martin and M. Giuliacci, University of Western Ontario, J. Hipfner and R. Moody, Laboratory Services Branch, Environment Ontario, Toronto, Ontario 735

VOLUME II

SESSION E: ENVIRONMENTAL SOCIO-ECONOMICS

Verbal Presentations **Page**

E2 **Tradable Permits for the Control of Sulphur Oxides in Canada;** C.D. Mallory, Environment Canada, Montreal, Quebec 740

E3 **Estimating Public Benefits of Implementing the Proposed Revisions to Regulation 308;** E.F. Haites*, Barakat & Chamberlin, Toronto, Ontario and P.A. Blyth, Environment Ontario, Toronto, Ontario 753

E4 **Recycling, Reducing and Reusing: A Theoretical Framework;** A.A. Kubursi* and D.W. Butterfield, Econometric Research Limited, Oakville, Ontario 765

E5 **The Economic Implications of the Zebra Mussel *(dreissena polymorpha pallas)* Invasion of the Great Lakes;** J.A. Donnan* and C.E. MacKay, Environment Ontario, Toronto, Ontario 775

E6 **Economics and Technical Change: The Water Resource Conundrum;** D. Tate*, Environment Canada, Ottawa, Ontario and R. Rivers, Environment Canada, Burlington, Ontario 790

E7 **Modelling Municipal Water Systems for Demand Management;** E.E. Creese* and J.E. Robinson, Environment and Resource Studies, University of Waterloo, Waterloo, Ontario 800

Volume II **Page**

E8 **Economic Analyses of Ontario's Water Pollution Control Initiative for Direct Industrial Dischargers;** O.E. Salamon*, J.A. Donnan, P.A. Blyth and L.M. Coplan, Environment Ontario, Toronto, Ontario 806

E9 **The Impacts and Effects of the Hagersville Tire Fire: Preliminary Analysis and Findings;** J. Eyles*, et al, McMaster University, Hamilton, Ontario (D. Sider, N. White, D. Willms, S.M. Taylor, D. Streiner, S. Walter, S. Elliott, J. Frank and M. Haight) 818

VOLUME II

SESSION F: MULTIMEDIA CONTAMINANTS & BIOTECHNOLOGY

Verbal Presentations **Page**

F2 **Regulating a Multi-media Contaminant: US EPA's Lead Strategy;** R. Levin, Environmental Protection Agency, Washington, D.C., USA 830

F3 **Application of a Multimedia Risk Assessment Approach to Ontario Soil Contamination Cases;** S. Fleming*, Hazardous Contaminants Coordination Branch, Environment Ontario, Toronto, Ontario 839

F4 **A Fugacity Model of Chemical Fate in an Uncertain Multi-media Environment;** D. Mackay*, S. Paterson and W. Stiver, University of Toronto, Toronto, Ontario 848

F5 **Pollutant Interactions in Mutagenicity Testing;** D.M. Logan* and A.S. Raj, York University, North York, Ontario 864

F6 **Genotoxic Compounds Associated with Respirable Urban Air Particulate. Chemical Fractionation and Bioassay of Complex Mixtures;** D.W. Bryant*, B.E. McCarry and D.R. McCalla, McMaster University, Hamilton, Ontario 874

F7 **Ministry Research Needs in Biotechnology;** J.S. Bailey, Hazardous Contaminants Coordination Branch, Environment Ontario, Toronto, Ontario 885

VOLUME II

KEYNOTE PRESENTATIONS

Keynote Paper I

Sustainable Development: The Technological Challenge

Noel J. Brown, Director, United Nations Environment Programme, North America

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"RESPONSES TO GLOBAL CHANGE:
the Coming Environmental and Economic Revolutions"

Keynote address: J. P. Bruce

Environmental Research: Technology Transfer Conference
Toronto, 19-20 November 1990

Extended Abstract:

The Intergovernmental Panel on Climate Change has provided in 1990, the most definitive scientific assessment to date of the changes in greenhouse gas concentrations in the atmosphere and the probable effects on the world's climate. This consensus report of more than 300 scientists from many countries, places the major conclusions in 4 main categories of descending degrees of scientific certainty. The Panel is *certain* that in the atmosphere and that human activities are substantially increasing greenhouse gas concentrations in the atmosphere and that the natural radiation exchanges known as the "greenhouse effect", are real. They "*calculate with confidence*" that CO2 has caused and will continue to produce more than half of the human-enhanced greenhouse effect, and that the long-lived gases, (CO2, nitrous oxides and the CFC's) would require immediate emission reductions of more than 60% to stabilize atmospheric concentrations at present levels. They *predict*, based on current model results, that if nothing is done, i.e. a "business-as-usual" scenario prevails, global mean temperatures will rise 0.3 degrees C per decade (with a range of 0.2 to 0.5 degrees C) and sea level will rise 6 cm per decade (range 3-10cm) over the next century. These are rates greater than ever experienced since man first tilled the soil, some 10,000 years ago. Northern latitudes and large land areas, like central and northern North America, are predicted to warm more rapidly than the global mean. The impacts of such changes on coastal communities, small islands, water resources, agriculture, forestry, the spread of tropical diseases, would be increasingly profound over the next 100 years. At their lowest level of certainty, they advise that their *judgement* is that the mean global temperature has already risen 0.3 degrees to 0.6 degrees C over the past 100 years, "broadly consistent with predictions of climate models".

Responses to this prospect have, on the one hand, been widespread alarm, especially on the part of low lying island countries and ones with extensive low coastlines, and countries with only marginal agriculture and water resources. Spokesmen for other countries, such as USSR, see a somewhat warmer climate as mostly advantageous. A number of western European countries, and scattered sub-national jurisdictions elsewhere have already announced plans to cut CO2 emissions, and some, including Canada, have committed themselves to a stabilization of emissions.

However, most agree that concentrated, coordinated international actions are needed to really reduce the rate of accumulation of greenhouse gases and attention is now focussed on negotiation of a global convention on climate change, hopefully by the item of the UN Conference on Environment and Development in Brazil, June 1992. The urgency is great, since as the IPCC points out, if nations can cut CO2 emissions by 2% per annum beginning in 1990, concentrations will be stabilized at 390 parts per million by 2020 or so, but if cuts are delayed 20 years, stabilization will not occur until 2070, and then at a much higher 460 ppm.

There are four major contentious issues which will have to be resolved in negotiations of a Convention on Climate Change. These are:

1) a plan to cut greenhouse gas emissions, especially CO2;
2) a plan to move from net global deforestation to afforestation;
3) transfer of funds or other economic incentives to permit developing countries to make the necessary investments and adjustments, and
4) transfer to developing countries on a preferred basis, of low emission technologies.

All of these issues have potentially enormous economic as well as environmental implications.

The first will require, above all, a major change in energy policies of the nations, especially the highest per capita energy users, Canada and USA. The key requirements are aggressive conservation strategies driven by end-use oriented services rather than the supply side, and switching to lower CO2 emitting fuels, away from oil and coal. Examples of what is achievable at low net cost in North America and India will be outlined.

In the business world, our major industrial competitors, in Europe and Japan, are already much more energy efficient than North America, and are adopting even greater efficiency measures. There is every reason to fear for the future competitiveness of Canada and USA if energy efficiency is not pursued vigorously in the next few decades.

The third of these issues is one stressed by developing countries in all of the pre-negotiation meetings. Without major initial financial investments, they will be unable to institute the energy efficiency, fuel switching and reforestation measures needed to prevent them from augmenting greenhouse gas emissions at a rapid rate to meet the increasing needs and expectations of their people. Such investments are clearly impossible in a world in which the net financial flow is away from the developing world with low commodity prices and huge debts, to the industrialized countries. This flow must be reversed, or at a minimum a major fund, greatly exceeding the $270 million committed to a CFC replacement fund, will be required to permit the developing countries to be full partners in a world-wide effort to protect the global atmosphere.

The recent success of the world community, in agreeing to a strengthened plan for CFC emission controls to protect the ozone layer under the Montreal protocol lends some optimism to the prospect of a more comprehensive climate change convention. It also buys a little time through CFC reductions to put in place the more difficult CO2, methane and nitrous oxide controls.

However, the major issues on the table can only be resolved if the industrialized countries accept their responsibility to greatly reduce their own greenhouse gas emissions, increase afforestation, and assist developing countries to do the same. Revolutions in our thinking about, and use of, energy, and in our relationships with developing countries are urgently needed if we are to protect the atmosphere of our small planet and the climate it produces.

VOLUME II

FEATURE PRESENTATIONS

A1

WHAT'S THE LATEST ON ACID DEPOSITION IN NORTH AMERICA?

Douglas L. Sisterson

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This presentation summarizes the results of the National Acid Precipitation Assessment Program State of Science/Technology Report Deposition Monitoring: Methods and Results (Sisterson et al. 1990). The larger document discusses methods to monitor wet, dry, and droplet deposition in the United States and Canada and provides temporal and spatial analyses for the period 1979-1987. A significant portion of the document addresses the representativeness and completeness of large-scale network deposition data at regional and local scales.

The most complete deposition monitoring results are for wet deposition. Information on dry deposition is insufficient to allow spatial and temporal analyses on a regional scale of the major acidic deposition species and their precursors. Information on droplet deposition (i.e., deposition by interception of cloud water and fog droplets, sometimes called "occult" deposition) is even more recent than that on dry deposition, and little information exists for spatial and temporal analyses except at a few sites.

The areas of maximum wet deposition of individual inorganic chemical species in precipitation are located in the northeastern United States and southeastern Canada, and those locations have not changed significantly in the past decade. The weight of scientific evidence suggests that all analytes except pH or acidity exhibited a decreasing (not statistically significant) trend in deposition and concentration in 1979-1987 for the eastern half of the United States and Canada. Median annual precipitation-weighted concentrations are larger in North America than in remote regions of the world by factors of 9 for SO_4^{2-}, 14 for NO_3^-, 7 for NH_4^+, and 4 for H^+. The average pH of precipitation in remote regions of the world is closer to 5.0 than to 5.6. Excluding precipitation monitoring sites from urban areas and the influence of major local sources causes the integrated wet deposition chemistry estimates to be low.

The finding that sulfur and nitrogen species in precipitation have decreased but pH has not changed is perhaps the single largest surprise of the State of Science Report. A large decrease in calcium and other base cations offsets decreases in acid species in precipitation. The reason for the decrease in calcium is not clear. In part, it can be attributed to changes in agricultural practices, paving of rural gravel highways, and perhaps emission controls; the same emission controls that remove sulfur and nitrogen species from smokestacks may also remove base cations such as calcium that reduce precipitation acidity.

Preliminary results indicate that dry deposition for sulfur is between 0.3 and 0.5 of the wet plus dry deposition at regionally representative sites and is between 0.3 and 0.7 for nitrogen. Most of the dry-deposited sulfur is due to SO_2, with values of 50-90%. Most of the dry-deposited nitrogen is due to HNO_3, with values of 76-88%. The ratio of dry plus wet deposition of sulfur species to that of nitrogen species varies between 4.25 and 0.77.

Concentrations of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ are 5-20 times larger in cloud water at high-elevation sites than in precipitation. Droplet deposition of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ is up to three times wet plus dry deposition in the warm season for high-elevation sites that are frequently in cloud. High-elevation sites above 900 m experienced in-cloud conditions 30-40% of the time during the growing season (April-October). The liquid water content averaged about 0.20 g m^{-3} at most sites.

By using these wet, dry, and droplet deposition data together with anthropogenic emissions and an estimated urban perturbation factor for wet and dry deposition, S and NO_x-N mass budgets were determined (Venkatram et al., 1990). For all of the United States and Canada combined, 39% of anthropogenic SO_x-S emissions were accounted for by wet deposition, 23% by dry deposition, and 4% by droplet deposition, and 34% of the emissions were exported from North America. For NO_x-N, 40% of anthropogenic emissions were accounted for by wet deposition, 26% by dry deposition, and 3% by droplet deposition, and 34% of the emissions were exported from North America. The urban perturbation accounts for 15% of the wet plus dry deposition for the United States and Canada combined.

It is interesting to note that both sulfur and nitrogen species in precipitation in Canada in this study exceed Canadian emissions, probably due to the overall net transport of emissions from the United States into Canada.

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A10 Measurement of Semi-Volatile Organic Compounds in Ambient Air; G. Hunt, ENSR, Acton, Massachusetts, USA

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ABSTRACT

Leach, J.H., Ontario Ministry of Natural Resources, Lake Erie Fisheries Station, R. R. #2, Wheatley, Ontario, N0P 2P0. Influence of the zebra mussel, Dreissena polymorpha on water quality of Lake Erie.

The European zebra mussel, Dreissena polymorpha (Pallas), is now well established in the Great Lakes system. Initial colonization may have occurred in 1986, likely from larvae discharged in ballast water, but mussels were not observed in Lake St. Clair and Lake Erie until June 1988. Large populations of the mussel are now established in these lakes. It has spread to all of the Great Lakes and is found from Cornwall, Ontario, in the east to Duluth, Minnesota, in the west. Dispersion has been aided by a motile larval stage and the ability of adults to attach to boat hulls with byssus threads.

The zebra mussel is a serious biofouling pest in Europe and is rapidly becoming one in North America. One of its most harmful impacts is the colonization of intake cribs and pipes serving water treatment plants, power generating stations and industries. Costs associated with prevention of infestations and removal of encrustations are projected at many millions of dollars.

Ecological impacts are also possible but are more difficult to predict and quantify. There is concern that some species of native mussels, and in particular the large unionids, may be in jeopardy because their shells are being colonized to the point where the mussels can no longer function normally. Although impacts on fisheries have not yet been measured, managers are concerned that the invader could affect fish production in two ways. The fouling of spawning reefs could affect reproduction of shoal spawners if the habitat is altered sufficiently to reduce egg deposition and survival. Preliminary results from observations on walleye in the western basin of Lake Erie indicated that reproduction and survival in 1990 were satisfactory. Secondly, the shifting of organic matter from pelagic to benthic areas through filtering by zebra mussels could disrupt the food web that links primary production to larval fish. Research to quantify this process and to determine its impact on the food web is currently underway in Lake Erie.

The zebra mussel has already affected water quality in Lake Erie and Lake St. Clair. The most visual impact is an increase in water clarity. Between 1988 and 1989 (May to November), mean Secchi disc transparencies increased 85 percent and 52 percent in the western and central basins of Lake Erie respectively. Preliminary data to September 1990 indicate that mean transparencies in 1990 were still greater than those in 1988 but less than those recorded in 1989. Resuspension of bottom sediments due to above normal winds during spring and early summer of 1990 probably masked the effects of the zebra mussels on water clarity. For example, transparencies in the western basin in August and September, 1990, were above those measured in the same period in 1989. Turbidity in Rondeau Bay has declined to the point where water clarity is probably sufficient to permit rooted aquatic plants to reestablish.

Mean concentrations of chlorophyll a declined 43 percent and 27 percent in the western and central basins of Lake Erie respectively between 1988 and 1989 (May to November periods). Preliminary results indicate a further decline in 1990, especially in the western basin. Dreissena is obviously competing successfully with filter feeders for phytoplankton. The production of faeces and peuedofaeces by Dreissena should favour other benthic organisms and early observations indicate an increase in gammarids in western basin reef areas. There is concern that a build-up of organic matter in the interstitial areas around the mussels could reduce dissolved oxygen concentrations through decomposition to the point where survival of fish eggs was adversely affected. However, a joint study with the Department of Fisheries and Oceans in April, 1990, indicated that dissolved oxygen was at or near saturation levels on walleye spawning reefs in the western basin of Lake Erie. Further studies are required to determine what happens to oxygen concentrations as organic matter and layers of mussels accumulate.

There are early indications that water taste and odour may be affected at water treatment plants (WTP) by Dreissena. Taste and odour problems occurred at the Windsor WTP in the summer of 1990 and were attributed to Dreissena either directly from the bodies of veligers and adults or indirectly from increased populations of aquatic plants because of improved water clarity. Additional research is required to delineate causes of taste and odour problems and also to determine to what extent Dreissena is improving water quality by concentrating contaminants.

CROSS-DISCIPLINARY ANALYSES OF ENVIRONMENTAL HEALTH STUDIES SUGGEST THE NEED FOR NEW APPROACHES TO RISK ASSESSMENT

by

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A comprehensive examination of the literature on wildlife and human health in the Great Lakes basin provides incentive for new approaches to assess hazard from exposure to bioaccumulative, toxic substances. A review of the mechanistic actions of the contaminants commonly found in wildlife and human tissue further supports the need for change. Current public health strategies to measure population effects are too blunt to detect the subtle health decrements that may occur as a result of exposure to these chemicals. Breakthroughs in understanding the effects of a number of these persistent, pervasive organic chemicals are being made in the Great Lakes region by integrating research in wildlife, human, veterinary, and animal toxicology, ecology, epidemiology, and cellular and tissue biology. Following years of monitoring contaminants in the ecosystem, researchers in these disciplines are beginning to interpret what the concentrations mean in terms of wildlife health effects. This information provides new tools for public health authorities to assess the status of human health.

Sixteen top predator species in the Great Lakes basin have experienced severe reproductive problems accompanied by population declines since the 1950s. The health of many bird species showed marked improvements in the 1970s as the result of reductions in DDT and its metabolites producing thicker egg shells and improved reproductivity. Today, health problems that are just as serious but far more subtle than eggshell thinning are still reported in top predator species. Few overt symptoms are reported in adult animals -- instead, they are observed in offspring of exposed animals.

Health problems observed in wildlife offspring have been associated with elevated exposure to a number of contaminants. Researchers infer this exposure is the result of parental transfer through the egg, placenta, breast milk, and/or feeding of contaminated prey to offspring. Anomalies reported in wildlife offspring include: metabolic problems that cause low birth weight, loss of weight gain, and in some instances death from wasting; edema; birth defects; embryo, chick, fetus, neonate, and young adult mortality; behavioral changes; target organ damage; immune suppression; and abnormal sexual development.

An examination of the literature on the chemicals most often found in both Great Lakes wildlife and human tissues was undertaken. With one exception, (benzo a pyrene) these contaminants are not acute toxicants and genotoxicants, nor have they been determined unequivocally to be human carcinogens. They are developmental toxicants. Research at the cellular and tissue level shows that the mechanisms of action of the critical Great Lakes pollutants are often similar and general in nature. Most of the critical chemicals found in elevated concentrations in Great Lakes biota are capable of affecting normal metabolism and development in at least one or all of the following ways. First, they block cell to cell communication. Second, they induce enzymes in a number of tissues that enhance the excretion of hormones naturally produced by the endocrine system. And third, because of their chemical structure they have an estrogenic influence as well. All three mechanisms under proper timing and dose can lead to abnormal development. The cumulative effect of mixtures of these chemicals at the cell, tissue, and organ level is just beginning to be understood.

It is important to note that in laboratory animals a number of developmental health decrements have been associated with specific PCB, dioxin, and furan congeners and a number of pesticides including DDT and its metabolites, dieldrin, lindane, hexachlorobenzene, and others. These adverse health effects include wasting, edema, birth defects, immune suppression, target organ damage, effeminization of male animals, behavioral changes, and premature death, all in a dose-related manner; the same health decrements reported in Great Lakes wildlife.

Most importantly, except for a few fish species and the Beluga whale, cancer has not been reported in Great Lakes animals. Unfortunately, most risk assessments are based on cancer, not developmental effects, with the exception of mercury and lead.

A global search of the literature on residues of these contaminants in human tissues reveals they are found in all reproductive tissue, including breast milk. As a result, exposure during the embryo, fetal, and perinatal periods can be elevated on a weight to weight basis, coinciding with a period of rapid development that sets the course of development through maturity. Recent laboratory studies using a number of these chemicals revealed that obvious health effects may not be fully manifested until adulthood in exposed animals. Using wildlife and animal studies as models to assess human health, new technologies are needed to measure human exposure as well as new approaches to measure the possible cognitive, behavioral, and social effects of developmental toxicants.

C1

ENVIRONMENTAL CONCERNS - KEEPING OUR PERSPECTIVE

John P. Nunan, P.Eng., President
Trow, Dames & Moore

INTRODUCTION

This talk is intentionally provocative. The purpose of the presentation is to put before you a number of current, relatively high-profile, environmental concerns, and to discuss these in brief so as to stimulate thinking as to the type of research that might be undertaken to enhance knowledge of these issues, and putting them in truer perspective as they may affect public health and safety, and the quality of our physical environment.

Four concerns (issues) have been selected for discussion, not necessarily because of their importance, but rather due to the fact that these issues have been around for some time with little growth in our understanding of their true significance and seriousness. They are also issues that are causing much concern to various segments of the community and expenditures of large amounts of money to mitigate, possibly with less than adequate understanding as to why or if such mitigation is effective, or really required.

As Professor P.H. Jones has said, "society is engulfed in fear". This fear is not based on scientific findings, which have demonstrated that harm can result. It is based more on our ability to detect certain substances in our environment which we have discovered can adversely affect humans if ingested in large quantities. It is wrong to equate, in the minds of the public, the mere detection of a substance with ghastly public health threats. Such concerns have tremendously complicated life and in several instances have brought some forms of desirable development to a grinding halt. Some specific issues causing these concerns will now be discussed.

1) Methane Gas

Methane is a naturally occurring light hydro-carbon gas that results from the biodegradation of carbonatious material in the absence of oxygen. Methane is very widespread in nature and comprises approximately 95 percent of natural gas. Methane is produced in significant quantities during anaerobic decomposition of solid wastes in garbage dumps. It is also produced in earth fills where relatively small quantities of biodegradable material such as grass, brush and swamp debris has been incorporated in the fill. Methane can migrate from its location of generation to accumulate in buildings and other works where ignition of the gas has resulted in destruction of buildings and loss of life.

Today, the measure of a methane hazard or risk is usually determined by the insitu concentration of the gas. Is this appropriate? Is there a better way to evaluate the hazard? Is it really necessary to restrict development as much as we now do because of the presence of high insitu concentrations of methane? Are there, or can there be developed reliable methods of measuring methane flux directly, which, when compared to conservative estimates of building ventilation, will show when a buildup of methane is so improbable that development of a particular site should not be constrained?

The issue of methane recovery from large, or even small garbage dumps, seems to offer a potentially attractive opportunity for energy recovery. This is already being achieved at some very large landfills, where the cost of energy is high and a suitable market for that energy is available. Some of the questions that need to be answered through research include: What are the conditions that enhance the rate of methane production? Is it better to keep landfill dry so as to restrict the rate of methane production, which also delays stabilization of the landfill, or is it preferable to develop sanitary landfills so as to enhance methane production? How would the recovery and use of methane from a landfill, where methane production was intentionally enhanced, compare economically with other forms of waste recycling for energy, conservation and recovery, such as the burning of refuse-derived fuel from waste? What do we know about the character of the solid waste that goes into our Canadian landfills? Are we perhaps missing opportunities or even aggravating conditions by some current practices such as removal of materials from waste streams that would produce methane, when the cost of reusing these materials in other ways is less attractive?

2) Nitrates In Groundwater

Nitrate which is an essential compound for plant growth and which is naturally produced in the environment by bacterial activity and to a much smaller degree, by electrical storms in the atmosphere, has become a major concern relative to the potable use of groundwater. The use of nitrate in fertilizers to increase food crop yields in rural areas and the heavy use of nitrogen fertilizers to grow green lawns in urban areas is increasingly suspected as being the cause of nitrate buildup in groundwater, which in many areas has risen to fifty percent, or more, of the accepted 10 ppm for drinking water. This change has caused concern that the trend will continue, which in turn has resulted in rejection of some well supplies intended for municipal use, even though all other quality and quantity factors are favourable. The limit of 10 ppm has been conservatively accepted as a safe limit for consumption by infants who are more susceptible to nitrates than are older children and adults. A question we should perhaps ask is: should these sources of water supply be rejected because of an increasing nitrate trend, when the content is still well below the accepted health standard? Does the trend mean that the nitrates will in fact rise above the limit? It can be shown that the use of fertilizer for cash crops will theoretically increase nitrates in groundwater over broad areas of intensively cultivated land by as much as five parts per million, but that level should not rise much higher under prevailing climatic conditions. The level of nitrate in water at a specific sampling point may not establish the content in the water from a heavily pumped well that draws water from a broad area of one or two square miles. Do we really know at what level nitrates significantly affect the health of humans? Can we demonstrate by research how significantly agricultural fertilizer affects groundwater quality? Are we rejecting plentiful supplies of water because of concerns over nitrate buildup and trace amounts of other agricultural chemicals where detailed study may show that this is unnecessary?

3) Landfill Leachate

Leachate is produced in landfills when precipitation percolates through buried solid waste, when waste is deposited below the water table, or when the water table rises into waste because a thick pile of slowly permeable waste alters the local hydrologic regime. Dissolved in landfill leachate are constituents of virtually everything that is in the waste itself and indeed some compounds that are produced by the mixing and interaction of solutes from waste. Leachate is for the most part, produced under anaerobic conditions and has a putrid odour. Because leachate contains many known, and suspected but unknown, water pollutants, great emphasis has been placed recently on the containment of landfill leachate by lining garbage dumps, and attempting with no proven success to cover them so as to restrict infiltration of precipitation. Recognizing that leachate accumulates, it is drawn off and disposed of in waste water treatment plants. Unfortunately, very little hard data exist on how effectively leachate is renovated by conventional secondary waste water practices. We know that BOD is reduced. We know that VOCs are removed; but to where, to the atmosphere? What is the fate of soluble inorganics? They are undoubtedly diluted before release to surface streams, but do they still persist to impact surface water?

Is secondary waste water treatment really superior to the attenuation treatment and dilution that takes place naturally in the soil beneath and around landfills as the leachate is carried slowly by groundwater? We know from experience that leachate contaminated groundwater beneath some very large landfills is renovated by natural processes within a few hundred metres of the landfill. Is this a legitimate use of a small segment of the natural environment? We know the effect will not be permanent. Have we made any quantitative studies to compare the effectiveness of natural subsurface treatment with conventional waste water treatment practices? What are the cost implications? Are we creating problems by making our waste dumps too large? Do we in fact know how seriously leachate affects health? Are there any authentically documented cases to show that waste residues in groundwater affected by landfills have actually made people sick? What evidence have we that artificial containment systems actually stop leachate escape permanently?

In summary, are garbage dumps the alleged monstrous insult to the environment they are thought by many to be, or do they indeed represent a legitimate, temporary use of very small segments of the physical environment? The actual land area used for sanitary landfill is relatively small in spite of the popular contention that we are burying ourselves in our own waste. Have you ever, on a clear day flying for one hour between Montreal and Toronto tried to locate the sanitary landfills? It is difficult, because they are on that scale very small and far between. If we attempted to prove that landfills are a legitimate land use rather than to look microscopically at their adverse effects, might we discover something useful?

4) Soil Classification Criteria For Landfills

In Ontario, disposal criteria have been developed which are designed to control the chemical quality of contaminated soil that, under Ontario Regulation 309 and the Decommissioning Guidelines, must be removed from decommissioned sites. Unfortunately, these rigourous criteria have caused a lot of inert material to be diverted to expensive and already severely burdened sanitary landfills, when much of the material would be perfectly safe if left where it was, or used to "make ground" for useful development. If the soils are classified as registerable waste or subject waste, the transportation and disposal cost in the Toronto region may range from $80.00 to $250.00 per tonne, depending upon the haul distance and character of the material.

The definition of inert fill is so broad that what constitutes inert is often a matter of opinion. Operators of "clean fill" sites are frequently unwilling to accept material if there is doubt as to its origin or chemical content. As a result, sites for disposal of marginally contaminated soil are very scarce.

Prior to acceptance by a municipal landfill, chemically contaminated soil of the type described above must be classified according to Ontario Regulation 309. The Regulation 309 classification procedure involves an acid leach test and comparison with criteria set out in Schedule 4 of the Regulation. Soils that leach less than 100 times (X) the Schedule 4 criteria are acceptable at a municipal landfill subject to further classification as to whether the soil is non-registerable (<10X the criteria), registerable (10 to 100X the criteria) or inflammable.

In my opinion, key questions that need to be addressed; particularly, for soils that are classified as non-registerable are: Is disposal of such soils at a municipal landfill responsible management of scarce landfill capacity? Certainly, in the Toronto area this is a valid question; particularly, when such soil has not generally been utilized for daily cover but rather incorporated into the waste cells? A possible answer may be that in the short term, revenue from receipt of materials classified as waste is considerably higher than materials received for top cover.

Is the current Regulation 309 leachate extraction procedure a proper method of evaluating disposal options for marginally contaminated soils in southern Ontario where conditions are naturally alkaline and where mono disposal of such soils would seem to be the preferred and most cost effective disposal option?

C10 Oxidation to Remove Trichloroethylene from Soil; G. Farquhar, University of Waterloo, Waterloo, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

D1

ION MOBILITY SPECTROMETRY IN ATMOSPHERIC ENVIRONMENTAL MONITORING IN THE US SPACE PROGRAM,

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ABSTRACT

The utilization of chemical instrumentation, originating with military establishments, for monitoring atmospheric environmental quality in domestic and space applications represent a little known and potentially rewarding example of technology transfer. Human exposure to hazardous airborne organic vapors at trace levels presents challenges in areas of risk assessment, toxicology, and technology of chemical sensing. Since ca. 1965, improvements in laboratory tools for measuring contamination have kindled interest in health effects from exposures that previously were disregarded. Still, refinements in toxicology, risk assessment, and human protection in those instances were dangers are certain have been hindered by limitations in chemical analysis of environmental and biological samples. While extraordinarily advanced tools for chemical characterization of samples are available, the expense and associated mechanical or electrical requirements of such instruments preclude uses in routine or continuous manner. As a result, the philosophy of environmental analysis has remained stagnant for the last two decades in spite of impressive sophistication of chemical instrumentation. A shift toward continuous monitoring or at least small portable chemical instrumentation is necessary and has been hindered only by the inherent properties and behavior of available technologies for chemical sensing.

Ion mobility spectrometry (IMS) is a derivative technology of a family of ionization detector based upon the conversion of hazardous vapors to ions in air at atmospheric pressure. In IMS, the ions are largely intact, though ionized, molecular species that can be analyzed for speed of movement in a weak electric field. This speed or ion mobility provides a measure of individual chemical constituents through the relationship of size-to-charge rather than mass-to-charge used throughout mass spectrometry. Thus, IMS can be viewed as an advanced smoke alarm where the ionization of atmospheric contaminants is followed by a rapid determination of the physical or chemical characteristics of the same ions. Advantages to IMS, in principal, include small size, low power, and trace detection limits but these were not realized until 1985.

Early developments of modern IMS can be dated to ca. 1965 when a military contract resulted in prototype hardware designs. Commercial versions were publicized in 1970 and several research groups, each with a particular developmental or investigative emphasis. Despite the demonstrated favorable response of IMS toward an impressive range of chemical classes, IMS was regarded widely as potentially significant but with serious limitations in selectivity and reliability. Studies during the last decade have shown these reservations to be rooted in the particulars of mechanisms of ion formation at atmospheric pressure rather than in ion mobility measurements.

Extensive in the consideration of IMS for environmental monitoring was the decision by the US and UK defense establishments to refine IMS for chemical warfare agent detection on battlefields. Ramifications in the use of instrumentation, formerly considered delicate and cumbersome, in such a hostile environmental included rugged, simple, and hand-held designs with refined ionization chemistry for integrity of response. In short, IMS was converted from a laboratory tool to a field monitor in a manner unlike any previous chemical analyzer. Present estimates of military distribution suggest an expansive role for IMS in armies of most western governments.

Instrumentation worthy of combat environments provided an impetus to explore civilian applications and in two instances found niches in the US space program. These two applications that are currently in testing or developmental stages include screening for vapors of hydrazines in the shuttle air lock and the use of portable gas chromatography/ion mobility spectrometry (GC/IMS) as a total hydrocarbon monitor for ambient air. In each instance, a fundamental obstacle to the utilization of IMS as envisioned and the primary emphasis of our research program has been the description and refinement of the chemistry of ionization. These will be discussed as used for the effective transfer of military IMS to environmental monitoring.

E1 Fostering Technological Transfer: Enabling Conditions in the Firm and in the Market; B. Hull, The Conference Board of Canada, Ottawa, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

UTILIZATION OF ENVIRONMENTAL RESEARCH TO CONTROL LEAD CONTAMINATION

by

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ABSTRACT

Due to the lack of well founded guidelines in the United States and other countries for lead contamination in soil, a special Society for Environmental Geochemistry and Health (SEGH) task force was formed to utilize research data and actual case studies to develop a report on recommended guidelines for Lead in Soil. An action oriented plan on how to systematically evaluate lead contamination for the protection of public health or determine lead levels to be used for remedial actions will be presented with examples of how to determine action levels for control or remedial measures associated with lead contamination problems.

INTRODUCTION

Technology transfer is a scientific terminology that implies many different interpretations dependent upon how it is used. In the United States, the Federal Technology Transfer Act (FTTA) of 1986 was passed to help remove perceived barriers for collaboration and utilization of research between the public-private sector. The preamble to the FTTA bill also noted that "many new discoveries in science occur at universities and federal laboratories while the application of this knowledge depends upon industry." (Nichols, 1990). However, technology transfer is often easier to propose than to implement due to the following constraints:

1. Cultural resistance encountered within countries and specific locations.
2. Time requirements before profit payback.
3. Necessity to also transfer appropriate training to carry out new technology.
4. Uncertainties of legal or regulatory requirements.

Our present time of environmental awareness has received further intensification by current environmental crises (such as the Alaskan oil spill, etc.), so that the public demands a more rapid transition of environmental research methodologies into practical applications. One major difficulty is how to evaluate research and transfer selected laboratory or field methodologies as rapidly as possible into a new or improved technology. For example, in Canada, the proposed process of converting sewage sludge into fuel, has the potential of replacing over 700,000 barrels of oil at a possible savings of over $28 Million at present oil prices which may continue to increase in the present unstable geopolitical mideast crisis (Nichols, 1990). While this may serve as a good model to illustrate technology transfer, industry is often reluctant to invest in many processes because of the difficulty in receiving government approval for the technology proposed. Environmental research may also be utilized for the development of guidelines such as the control of lead contamination and allow for the use of appropriate technology, including remedial actions, to be approved by public health officials and regulatory agencies for use by concerned industries.

USE OF ENVIRONMENTAL RESEARCH

The absence of scientifically recognized guidelines in the United States, as well as other countries, concerning the acceptable concentration of lead in soil (Davies and Wixson, 1987) has contributed to confusion by regulatory agencies, industries, public health officials, the medical community and concerned citizens (Lead in Soil, 1988). The questions most often asked focus on possible adverse health effects and risks from lead exposure or the recommended permissible soil lead concentration to be used for remedial action at contaminated or hazardous waste sites (Davies and Wixson, 1986).

Preventive measures or control technologies are usually not applied when there is an uncertainty of regulatory requirements. Therefore, environmental research data from around the world was utilized by a Society for Environmental Geochemistry and Health (SEGH) task force in developing a report on recommended guidelines for "Lead in Soil" (Wixson, 1988). This report illustrates how cooperative efforts between industries and regulatory officials may be applied to determine the risk of human exposure to lead (Davies and Wixson, 1989). The methodology used in this report also shows how environmental research can be applied to develop guidelines necessary for the application or control of remedial technologies.

The SEGH task force was formed in 1988 to address the problems, evaluate data and develop scientific recommendations concerning lead in soil. The risk assessment steps of: 1) hazard identification; 2) dose-response assessment; 3) exposure assessment; and 4) risk characterization were used develop a "Phased Action Plan" (illustrated in Figure 1) which evaluates the relationship between blood lead levels and the levels of lead in soil as one possible source of exposure. The "Phased Action Plan" also required extensive review of research data and case studies for the development of a target soil lead/dust lead guideline model derived from the use of documented health criteria.

The factors associated with Lead and Health are concerned with the population groups at risk from the possible adverse health

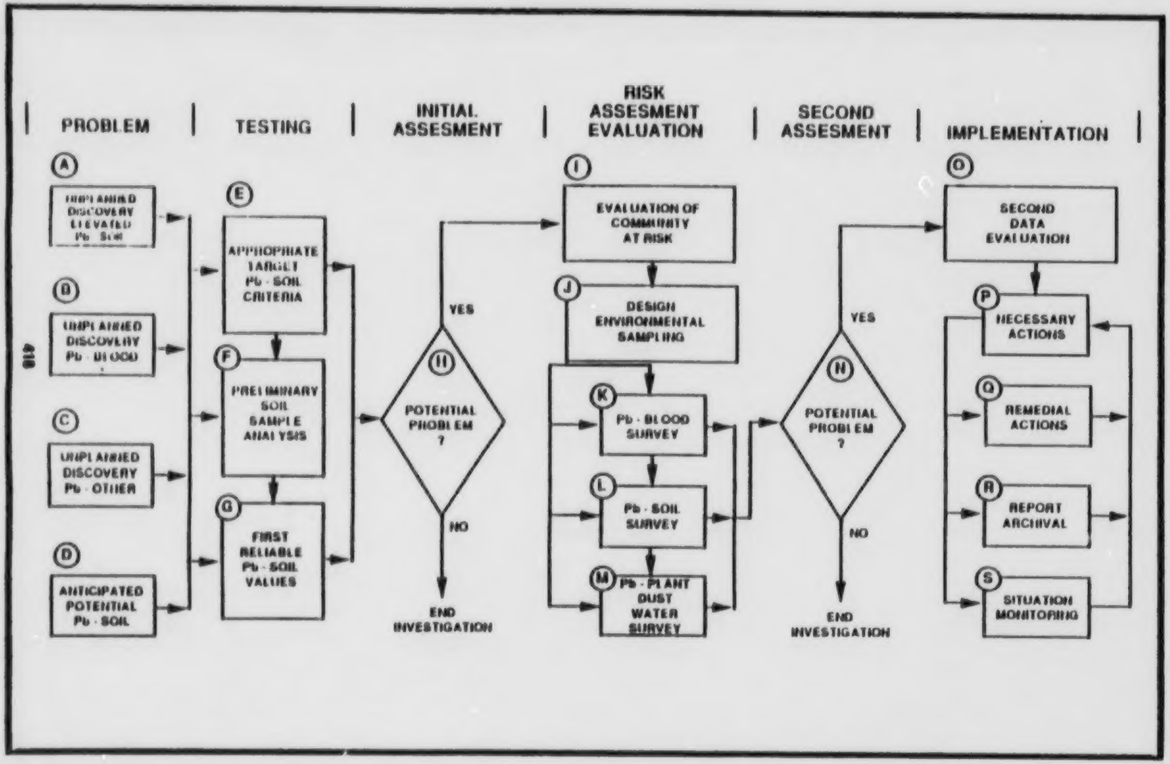
PROBLEM
TESTING
INITIAL ASSESMENT
RISK ASSESMENT EVALUATION
SECOND ASSESMENT
IMPLEMENTATION
A
UNPLANNED DISCOVERY ELEVATED Pb · SOIL
B
UNPLANNED DISCOVERY Pb · BLOOD
C
UNPLANNED DISCOVERY Pb · OTHER
D
ANTICIPATED POTENTIAL Pb · SOIL
E
APPROPRIATE TARGET Pb · SOIL CRITERIA
F
PRELIMINARY SOIL SAMPLE ANALYSIS
G
FIRST RELIABLE Pb · SOIL VALUES
H
POTENTIAL PROBLEM ?
YES
NO
END INVESTIGATION
I
EVALUATION OF COMMUNITY AT RISK
J
DESIGN ENVIRONMENTAL SAMPLING
K
Pb · BLOOD SURVEY
L
Pb · SOIL SURVEY
M
Pb · PLANT DUST WATER SURVEY
N
POTENTIAL PROBLEM ?
YES
NO
END INVESTIGATION
O
SECOND DATA EVALUATION
P
NECESSARY ACTIONS
Q
REMEDIAL ACTIONS
R
REPORT ARCHIVAL
S
SITUATION MONITORING

Figure 1. Phased action plan for lead in soil

effects of lead. Therefore, health criteria and research data were used in deriving a target soil/dust lead guideline concentration.

A single number for a lead in soil guideline for the protection of young children was considered unrealistic for a number of reasons. The population at risk can itself vary; therefore, the soil/dust guideline was established as a relationship or formula, in order to allow for a variety of environmental situations and regulatory criteria.

In the model developed, blood lead concentration was equated to a baseline level plus an increment resulting from exposure to soil or dust lead. The model also takes account of the chosen blood lead guideline or target concentration and the degree of protection requred for the population. The slope of the blood lead-soil lead relationship is then used in calculating an increase in blood lead over a baseline value. Hence the soil guideline, can vary depending on a variety of factors, allowing this response to be adjusted for a given situation with the opportunity of being modified as more research data become available.

The derivation of the blood lead/soil lead model is illustrated in Figure 2.

The major uncertainty in the use of such a realtionship is the value to use for δ , the response of blood lead to increasing soil or dust lead concentration. It therefore appears that a value in the range of 2-5 would be appropriate for most siutations and that the major influence on a value for δ may in fact be child activity rather than any characteristics of dust or soil.

RISK MANAGEMENT

The risk management section of the SEGH report emphasizes the exposure assessment and development of a relationship between blood lead levels and the concentration of lead in soil to formulate suggested guidance for acceptable soil lead. Geographic and physical processes that affect soil lead accumulation are discussed along with social aspects of lead contamination and other risks.

Legal aspects and cleanup levels for lead are presented along with economic considerations of appropriate technology utilized for remedial actions.

SUMMARY

The lack of guidelines or regulations often contribute to difficulties in implementation of improved technology for the control of metal contamination. The use of environmental and human health research data coupled with case studies of lead contamination have been used by a SEGH task force to develop a

TARGET SOIL/DUST LEAD GUIDELINE MODEL
DERIVED FROM USE OF HEALTH CRITERIA

$$S = \frac{\left| \frac{T}{G^n} - B \right|}{\delta} \cdot 1000$$

where:

S is the soil or dust guideline, a geometric mean concentration in µg Pb per gram of dust (ppm)

T is the blood lead guideline or target concentration, in µg Pb/dl whole blood

G is the geometric standard deviation of the blood lead distribution, typically in the range of 1.3 to 1.5

B is the background or baseline blood lead concentration in the population from sources other than soil and dust

n is the number of standard deviations corresponding to the degree of protection required for the population at risk, and would normally follow from the way in which the blood lead guideline T was defined

δ is the slope or response of the blood lead - soil(dust) lead relationship and has the units of µg Pb/dl blood increase per 1000 ppm increment of soil or dust lead

Figure 2.

Derivation of the blood lead/soil lead model report on recommended guidelines for lead in soil. These guidelines are necessary to control of lead contamination by recommending action levels to protect public health. Recommended levels of lead contamination in soil also may be used to determine how clean is clean? when remedial action is necessary.

ACKNOWLEDGEMENTS

The support of the Society for Environmental Geochemistry and Health, the International Lead Zinc Research Organization, Inc., the Lead Industries Association and the US Environmental Protection Agency is acknowledged. Special thanks also to the members of the Lead in Soil task force for their time and effort on this important project.

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VOLUME II

PANEL PRESENTATIONS

P1

"GLOBAL WARMING: WHAT IS AT STAKE? - Panel Discussion

THE INTERNATIONAL SCENE: J. P. Bruce

With the first assessment report of the Intergovernmental Panel on Climate Change (IPCC), and the Second World Climate Conference (SWCC) completed, discussion of greenhouse gases and climate change are now moving to a more formal stage of international negotiation of a Convention on Climate Change. The positions taken by various countries at the IPCC meetings and the debates at the SWCC give clear indications of some of the major issues that will have to be addressed in negotiation of a global Convention. These issues will be identified and some possible means will be suggested of addressing the diverse concerns.

Major changes in both environmental and economic policies, especially in the energy sector, will be needed in most countries if an effective international agreement is to be reached.

P2

GLOBAL WARMING: A CANADIAN PERSPECTIVE AND ACTION STRATEGY

Dr. D. Kirk Dawson
Director General
Canadian Climate Centre

Climate Change is perhaps one of the best examples of global interdependence of countries. An effective response will require a global effort which is likely to have considerable impact on human kind. A major dilemma, however, is that actions may be required well before many of the specific issues can be analyzed more thoroughly by further research.

Some of the more stringent actions that may be required, particularly those which serve to limit emissions of greenhouse gases, will have a profound effect on national policies in all areas. The manner in which nations address this issue will have major implications for trade and economic balance, between industrialized and developing countries, between industrialized nations themselves and within the different regions of individual countries.

Canada has played a significant role in seeking international solutions. We have been an active participant on the Intergovernmental Panel on Climate Change (IPCC) and are strong proponents of the negotiation of a comprehensive global convention on climate change.

At home, Canada supports a world-class climate research and impacts program and is now working with the provinces to conclude a National Action Strategy on climate change. The strategy will be:

- Comprehensive. It will deal with all of the major sources of greenhouse gases and the sinks of those gases;
- National in Scope. It will contain strategies appropriate for all levels of government, as well as industry and individuals, while recognizing that climate change is a global problem requiring international cooperation; and
- Action-oriented. It will be a cost effective and flexible action program that is based so that it can respond to new understanding and developments in the future.

P3

Global Warming: What Is At Stake?
Socio-economics

Erik Haites

In relation to global warming, socio-economics could cover many issues. To meet my time constraints, I must limit the scope of my presentation.

I will not discuss the socio-economic consequences of global warming, nor the socio-economic implications of adaptation to climate change. For Ontario, these were reviewed at a workshop organized by the A.E.S. in November 1985. A summary of that workshop is available in the Climate Change Digest (CCD 88-08) "CO_2 Induced Climate Change in Ontario: Interdependencies and Resource Strategies."

Today, I will focus on two socio-economic aspects of global warming that are the subject of more current research. They are:

- the costs of achieving reductions in emissions of greenhouse gases and
- the potential application of economic instruments to reduce greenhouse gas emissions.

Following the Toronto Climate Conference in June 1988, analysts started to examine how the proposed interim target of a 20% reduction in 1988 emissions of CO_2 by 2005 could be achieved. I reported on such an analysis for Canada at this conference last year. During 1989 and early 1990, studies were completed for a number of countries. The universal conclusion is that the Toronto Conference target is a tough one. Virtually, all currently available CO_2 emissions abatement measures will need to be implemented to their full technical potential to reach that goal.

Once the measures needed to achieve the target are known, people want to know the cost of implementing those measures. Although some preliminary answers are available, this is a matter that is currently under intense study.

The preliminary cost estimates range from about -0.3 to +0.5 percent of GNP annually to 2005. Some studies show net savings, as a result of lower energy consumption, from measures to reduce emissions of CO_2. Other studies show a net cost for these measures. The results tend to vary systematically with the methodology used.

Typically, energy efficiency, measures account for the bulk of the CO_2 emissions reductions to 2005. Studies that analyse the economics of individual energy efficiency measures, find most of these measures to be attractive from a societal perspective. They assume that the measures are implemented as part of the normal replacement cycle. This yields an overall saving as a result of implementing the CO_2 emissions reduction measures. Studies for Canada and Australia are good examples of this approach.

The other approach to estimating the cost of CO_2 emissions abatement is to use a macro-economic model. A carbon tax is used to achieve the target reduction in emissions. The tax revenues are recycled so that there is no net loss to the economy. Studies of this sort for the U.S., Japan, and other countries, all yield positive costs for CO_2 emissions reduction.

The carbon tax approach causes all energy users to adjust their energy consumption and equipment at the same time, reflecting the introduction of the tax. Adjustments do not reflect the replacement cycle for energy using equipment, thus raising the adjustment costs. On the other hand, assuming that all adjustments occur as part of the normal replacement cycle and that the adjustment costs of the equipment producing industries are reflected in the equipment prices, undoubtedly understates the adjustments. There are probably other reasons as well for the differences in the cost estimates produced by the two methodologies.

In any event, the first order estimates of the cost are between -0.3 and +0.5 percent of GNP. Research currently underway will refine these estimates and provide a better understanding of the nature and magnitude of the costs.

Economists believe that policies, such as emissions charges or tradeable emissions permits, can achieve a specified environmental target at lower overall cost than emissions regulations. Given the scale of the emissions reductions proposed by the Toronto Conference target, cost-effective policies are doubly important. I stressed the need for such policies in last year's session.

Tom Tietenberg and I have outlined a linked system of emissions permits and emissions taxes for carbon dioxide and other greenhouse gases. Briefly, the system is as follows. Each country is assigned emissions targets by international agreement; developing countries would probably have targets greater than current emissions and developed countries might have targets 25 percent below current emissions.

Within a country, such as Canada, large sources could earn permits for reductions beyond their target. Other large sources, such as industries, electric utilities, and large commercial and institutional facilities, could purchase permits in order to reach their target reduction. The fuels used by smaller sources, residences, vehicles, and small commercial facilities, would include an emissions tax equal to the market price of the permits. Thus, all sources have the same target reduction and the same cost per unit of CO_2 reduced.

International trade in permits would be allowed. However, each country could establish import and export restrictions. Developing countries could restrict trades between subsidiaries and parent companies if they chose. A country could restrict imports from countries whose permits it judged to be of dubious value. These arrangements provide economic incentives to participate in the international agreements for control of greenhouse gases. And, they provide enforcement mechanisms without requiring an international inspectorate.

The system, we believe, could be extended to CFCs, many sources of methane emissions and afforestation, but not to nitrous oxide, ozone, or ground level ozone precursors.

In conclusion, policy analysis of global warming is proceeding at a very rapid pace. Last year, the potential abatement measures and the scale of the response required were just being determined. They are now fairly well known and preliminary estimates of the associated costs are available. These cost estimates are being refined and appropriate policies are being formulated. Next year, I hope that we will know what policies are to be implemented in Ontario, in Canada, and internationally.

P4

WARMING TO A CRISIS:
THE MEDIA AND CLIMATE CHANGE

Abstract for a speech

By Michael Keating
Environment Writer and Consultant

to

The Technology Transfer Conference of Environment Ontario
Royal York Hotel
November 20, 1990

Global warming hit the front pages in Canada in October, 1983. This came immediately after the New York Times broke the story of the EPA report by John Hoffman, saying the greenhouse effect would begin in the 1990s.

This led to a small flurry of stories, which grew slowly but steadily into a trickle, and, over the last few years, into a flood.

The pace of coverage picked up in the mid-1980s as more of the big media, such as Time Magazine and the TV networks, caught on to climate change as a mega-story. There was talk of a threat to human life.

It was and is a great story for graphic images. Belching smokestacks and burning forests. Kentucky winters in Toronto. Glaciers crashing into the sea as the ice caps melt. Waves lapping at the doors of Wall Street. Two, three or four Prince Edward Islands. Florida going back the the alligators. Hurricanes with 40 to 50 per cent more punch than now.

People even coined the term "heat beat" for reporting on climate change.

The story got a real boost in 1988 when reporters had both the devastating heat waves in central North America and the Toronto conference on the changing atmosphere. And that was when James Hansen of NASA told the U.S. Congress that he was 99 per cent sure that climate change had begun.

The seriousness of the issue was reinforced by the record drop in the Mississippi River and ensuing calls from some U.S. politicians for water diversions from the Great Lakes.

So, how have the media covered the science of global warming?

Since the early 1980s, reporters have generally accepted that climate change is a real and poses a serious threat. They have given relatively little coverage to scientists, or politicians, who say this is just a theory.

I think reporters feel global warming is a fairly easy concept to grasp. Humans put billions of tonnes of gases into the atmosphere. Billions is a big number, so it must have an impact.

Reporters have generally treated climate change as a "bad thing" but that has not been universal. There are still some stories about the benefits of warmer winters and less snow.

How responsible have the news media been in reporting on global warming? By and large the reporting that I have seen has been fairly accurate. It has been much better than coverage of some issue such as PCBs.

But whether or not you like the coverage so far depends a lot on what hat you are wearing.

If you are a scientist who believes that global warming is a problem, then you are probably happy with the fact the media have made the greenhouse effect as common a phrase as acid rain. I think the environment movement feels the same way.

If you are a scientist who believes it is just a theory, then you probably feel the media have not been critical enough of the other scientific camp.

If you a minister of environment and have been in the portfolio long enough to understand the issues, then you probably like the coverage. You will hope that the media put more pressure on the premier or prime minister and the minister of energy to come up with greenhouse gas strategies.

If you are the minister of energy you probably wish the media would stick to covering the deficit or the ups and downs of the stock market.

If you work for the oil and coal industry you probably don't want to open your paper in the morning.

Where will news coverage go in the future?

The media are on to the fact that, per capita, Canadians are the world's greatest energy users and one of the world's greatest producers of greenhouse gases.

Where will the mud from this kind of coverage stick?

That's very hard to predict. A lot depends on the critics and on scientific research that is released to the public.

We have already seen considerable criticism of the coal-burning power plant at Point Aconi, Cape Breton, and some criticism of Hibernia in the east, and heavy oil projects in the north, because of they will all add CO_2 to the atmosphere.

There is an increasing number of stories about CO_2 from automobiles but the media have an ambivalent role in this one, since most reporters drive cars, and the media get a lot of revenue from auto ads.

The media face at least two difficult tasks ahead.

One will be in deciding when to report that global warming has started. The second will be in focussing on what to do about the problems.

Expert groups, including the Toronto atmosphere conference, suggested that the world should start switching to low or no carbon fuels such as hydro-electricity, wind, solar power, natural gas, biomass and possibly nuclear energy, if it can be made safe and if its use does not lead to more nuclear weapons.

We are also hearing calls from less developed nations for massive assistance to help them cut or avoid the emission of greenhouse gases while reducing poverty, hunger and disease.

These are complex stories, often without a clear set of targets to shoot at. Reporters are going to need lots of help from the scientists, policy makers, researchers, environment groups and others.

I remember quoting the Brundtland Report as saying we need lifestyles that are, "within the planet's ecological means." And I remember asking Maurice Strong if humans can make that kind of shift quickly enough. He said, "it is going to be a race between our sense of survival and our more indulgent drives."

What we need now is articulate spokespersons who will tell the public, through the media, how we are going to win that race.

* * *

P5

1990 TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 20, 1990

ABSTRACT OF J.D. McFARLAND'S REMARKS

The potential for global warming has become one of the most complex and hotly-debated issues in the energy/environment dialogue. Although there appears to be an emerging scientific consensus that an enhanced greenhouse effect is real, many uncertainties remain with regard to the magnitude, timing and regional effects. Canadians as yet do not fully understand the implications of this issue on public policy development nor the economic consequences of potential policy measures to address it. The energy industry is vitally concerned about promoting sound public policy in this area, and Imperial Oil has been active in providing a perspective on the issue in the context of domestic and international energy use. Imperial's initiatives to generate a broader understanding of the scientific and economic implications for Canada and Imperial are discussed.

J.D. McFarland/wl
October 5, 1990

P6

Global Warming: What's Known and What's Not?

Bunli Yang

Global warming and what industrialized societies might do about it have become topics of intense debate. Apart from its importance as an environmental issue, and it is often regarded the most serious threat to the global environment, global warming has many uncertainties. That kind of uncertainty generates debate and may be a barrier to action.

It is straightforward to list what is known about global warming and climate change:

- there is a natural greenhouse effect in our atmosphere because of gases that trap heat;
- the natural greenhouse effect accounts for a warming of about 33 C.;
- the climate of an ice age differed from today's by a small change in average temperature, about 5 C.;
- in the past, average temperatures and concentrations of the greenhouse gases have been high together and low together;
- human activities have been increasing the concentrations of the greenhouse gases in the atmosphere;
- the impacts on climate of rapid changes in temperature will not be uniform;
- climate is inherently global, and international agreement on actions will be very difficult.

The list of unknowns is, of course, endless. They range from the phsyical science of clouds and oceans to the economics and the social impacts of climate change. Examples are the rise in sea level for any level of greenhouse gas concentrations, or the rate of temperature rise, or the amount of precipitation and soil dryness because of any warming, or the costs of prevention, or the costs of adaptation to climate change. The risks of climate change, though not known or even knowable, are widely regarded to be major.

While these unknowns may loom large, uncertainties about usual economic trends are even larger, but are not barriers to economic policies and actions.

For purposes of public policy, the relevant question is not "How much needs to be known with high certainty before taking action?" but "What should be done now, by whom, in the face of the risks?"

VOLUME II

SESSION C

LIQUID & SOLID WASTE RESEARCH

VERBAL PRESENTATIONS

C2

MANUAL FOR ESTABLISHING VEGETATION ON EROSION-PRONE LANDFILL SLOPES IN ONTARIO

N. DeFraeye and T.W. Hilditch,
Gartner Lee Limited, Markham, Ontario

I Introduction

The Ontario Ministry of the Environment (MOE) was concerned with the problem of erosion on landfill sites throughout the province. Up until 1986 the extent of the problem had not been documented in Ontario.

In 1987, a three year study was undertaken by Gartner Lee Limited (GLL), commissioned under the MOE, the goal of which was to develop a practical approach to remediate erosion on landfill sites via proper vegetation establishment and management.

The end products of this study were:

- a technical paper documenting the problem of landfill cover erosion in Ontario, complete with the results of test plot revegetation research across the Province; and
- a Provincial Landfill Revegetation Manual for landfill operators to provide guidelines on the establishment and management of vegetation on landfill covers for the prime objective of erosion management.

II Study Approach

Our activities during the study, concentrated on three components:

- an overview of erosion of landfill sites in Ontario;
- identification of the best revegetation techniques; and
- establishment of demonstration plots throughout Ontario.

To gain an overview of erosion on landfill sites in the Province, a questionnaire was developed to solicit information from individuals who have first-hand exposure to landfills occurring in a range of conditions. The questionnaire was distributed to the Abatement Officers at 22 District Offices of the MOE throughout the Province. As their responsibility includes the enforcement of proper landfill management, it was felt they could provide a current and objective view on landfill erosion throughout Ontario. Responses to the questionnaire provided an appraisal of landfill erosion on 52 landfills throughout the Province. This was screened down to 24 sites (4 in each of the 6 MOE Regions) for the collection of physical and biological field data.

Concurrently, literature from throughout North America was reviewed, in order to gain an understanding of the problems of landfill erosion in other jurisdictions. As well, techniques for site preparation, planting, and maintenance were evaluated.

Initial fieldwork included a visit to the twenty four sites which had been selected to represent the wide range of geographic and physical settings in which landfills have been located in Ontario. The selected sites included both operating and closed landfills. Of the 24 sites which were examined, all of the open sites and 83% of the closed sites suffered from erosion problems. Our literature review indicated that the problem is not limited to Ontario.

III The Problem

Not only does the widespread occurrence of landfill erosion in Ontario cause aesthetic and operational concerns, it also fails to meet the requirements established by the Ministry of the Environment (MOE), for the operation and closure of landfills, as specified in the "Certificate of Approval."

IV A Description of the "How-To" Manual

The purpose of the manual produced during this study is twofold:

- to assist the landfill owner/operator with the remediation of erosion on landfill sites through the establishment and management of vegetation; and
- to assist landfill designers with the prevention of erosion with a successful revegetation program.

The manual is simple and straightforward to use. It includes five main components:

- inventory of problem areas and existing conditions;
- examination of problems, proposing solutions;
- planning a revegetation program;
- implementation of the program; and
- follow-up care.

The manual is targeted towards an expected user group which includes landfill operators, owners, regulators, consultants, and academics.

Following is a brief overview of the main components of the manual:

a) Inventory of problem areas and existing conditions

In order to resolve erosion problems and establish or repair a vegetative cover, the problems need to be accurately assessed.

Two systems were prepared to help the operator gather and record the information required to address the problem. The first is the "Problem Evaluation Check Sheet." It records the physical characteristics of the problem areas of the landfill for later analysis, and is intended to be completed on-site. The second system is a key, which presents `either...or' descriptions of existing vegetation (or lack of). The key provides a decision path for the operator to follow through to problem headings which are addressed in the text.

By completing the Check Sheet (Figure 1) in the field during regular site inspections and for special problem solving investigations, these can provide a valuable history of the landfill.

The Check Sheet leads the investigator through an examination of the physical factors that influence growing conditions on the landfill slopes:

- slope length
- slope steepness
- erosion types (sheet, rill, and gully)
- soil texture
- organic matter
- compaction, and
- low soil moisture.

Verbal and/or visual assistance is provided with the Check Sheet and in the text of the manual to assist an untrained investigator in undertaking the investigation.

The second aid, the "Key to Problem Identification" (Figure 2), is intended to assist in identifying problems related to the growth of vegetation on a landfill. Copies of the key are to be taken into the field. For each problem area, the investigator can proceed through the "decision path" based on observations of the existing vegetation, or lack of it. Each decision path leads to a factor which may be related to the poor vegetative cover. Since more than one factor may be contributing to the poor growth, it is possible that several decision paths can be pursued, to determine all related causes. These decision path factors are referenced to the text of the manual, in which detailed descriptions can be found, along with solutions. As with any document regarding the landfill, it is recommended that completed keys be kept as a record of problem occurrence and remediation on the landfill.

b) Examination of potential problems/ proposed solutions

The causes of erosion on landfill slopes can often be interrelated, and therefore, confusing to interpret. The manual examines the causes individually, first describing the problem and how to recognize it, then outlining how to overcome it.

The problems examined are:

- excessive slope length and steepness;
- existing erosion;
- unfavourable soil characteristics:
    - excessive compaction;
    - high or low soil pH;
    - poor texture;
    - lack of organic matter;
    - absence of available nutrients;
    - toxic levels of nutrients and/or chemicals; and
    - lack of moisture, poor moisture capacity;
- leachate seeps;

FIGURE 1: PROBLEM EVALUATION CHECK SHEET

1. **Instructions for Use**

Locate the problem areas on the landfill and sketch them on a copy of the site plan, an air photo, or on the attached diagram (Fig. 4). Using a check sheet for each problem area, check off the details that apply. Identify the different problem areas on the map as A, B, C, etc. and use the same coding on the check sheet.

2. SITE: ____________________ DATE: ____________________
INSPECTOR: ____________________ WEATHER: ____________________

3. Pace the distance from the toe to the top of slope, across the problem area. Take big steps, considering that each pace is 1± metre. More details can be found in Section 4.1.

SLOPE LENGTH
Long (150 to 300m) ____________
Medium (60 to 150m) ____________
Short (30 to 60m) ____________
Very Short (0 to 30m) ____________

Check off correct range.

4. Have an assistant stand on the slope or use a stick about 2m in length which can be stuck into the ground. From a view point about 20 metres away on the same level, estimate the distance from the top of your assistant's head horizontally to the slope, using their height as a unit of measurement. This will give you the Vertical to Horizontal ratio of the slope, ie. one unit of height vertically = two units of height horizontally. Fig.5 shows other ways to measure slope steepness.

SLOPE STEEPNESS

Check off closest range

Vertical : Horizontal
1 : 1 or Steeper ____________
1 : 2 ____________
1 : 3 ____________
1 : 4 or flatter ____________

5. On bare ground portions of the slope, look for:

* Upper layer of soil has washed away leaving exposed stones, sticks, debris.

* Surface runoff has cut small channels 0 to 10cm in the cover materials.

* Running water has cut one or more channels deeper than 10cm.

One, two, or three erosion types may be present on the same problem area. Refer to Section 4.2 for more details.

EROSION TYPES

SHEET EROSION:
Whole site* ____________
Limited area* ____________
Absent ____________

RILL EROSION:
Whole site* ____________
Limited area* ____________
Absent ____________

GULLY EROSION:
Present* ____________
Absent ____________

*Be sure to sketch on plan.

Check presence or absence of one or more erosion types, and note details such as length, width and depth.

FIGURE 1: (Cont'd).

6.	Using the soil texture field tests described in Appendix C of the manual, determine the soil texture, or collect small samples in plastic lunch bags and bring them back to analyse when you can refer to the test instructions. Remember to identify where the sample was taken, using the coding for the problem areas. Refer to Section 4.3.3 for further details.	**SOIL TEXTURE** Sand ________ Silt ________ Clay ________ Loam (topsoil) ________ Check or describe appropriate texture
7.	Look for dark soil colour with small bits of decaying leaves and roots. A small sample can be collected and labelled. When you get back, shake up the sample in a jar full of water. If there is organic matter in the sample, it will tend to float on the water in the jar. See also Section 4.3.4.	**ORGANIC MATTER** Present ________ Absent ________ Not Determined ________ Check presence or absence
8.	Observe whether the surface is smooth, hard, and/or difficult to push a shovel or stick into. This is further described in Section 4.3.1.	**COMPACTION** Yes (hard) ________ No (softer) ________ Not Determined ________
9.	The presence of cracks,or soil blowing into drifts, usually indicates dry conditions. Refer to section 4.3.6. for description.	**LOW SOIL MOISTURE** Yes ________ No ________ Not Determined ________

KEY TO PROBLEM IDENTIFICATION

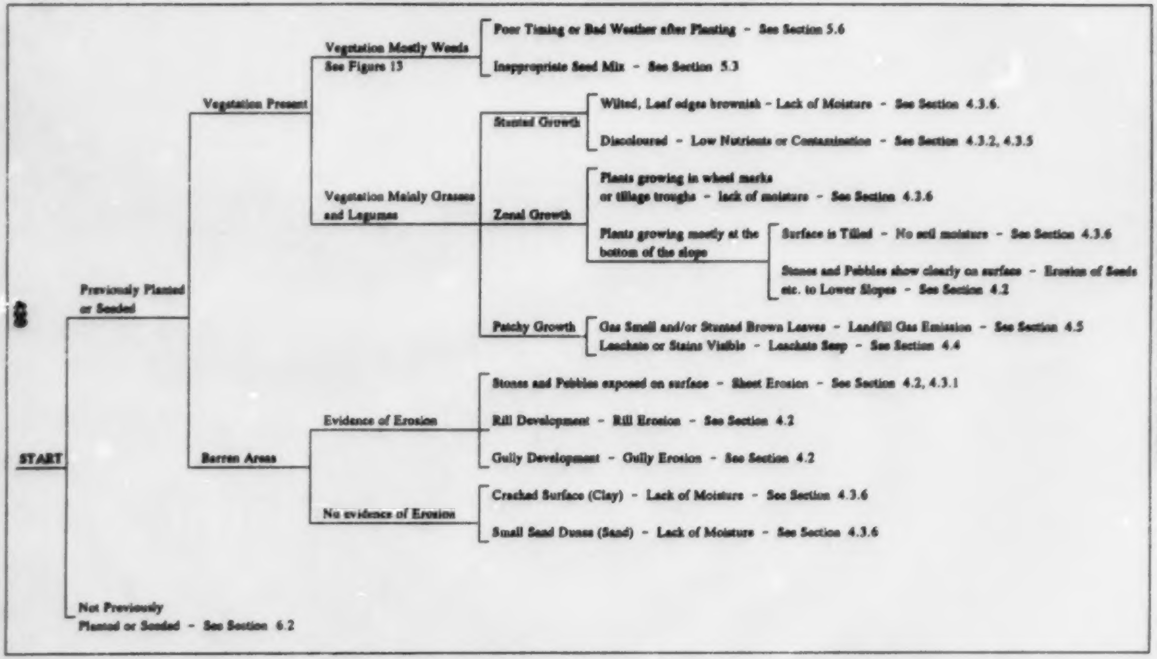
START
Previously Planted or Seeded
Vegetation Present
Vegetation Mostly Weeds See Figure 13
Poor Timing or Bad Weather after Planting - See Section 5.6
Inappropriate Seed Mix - See Section 5.3
Vegetation Mainly Grasses and Legumes
Stunted Growth
Wilted, Leaf edges brownish - Lack of Moisture - See Section 4.3.6.
Discoloured - Low Nutrients or Contamination - See Section 4.3.2, 4.3.5
Zonal Growth
Plants growing in wheel marks or tillage troughs - lack of moisture - See Section 4.3.6
Plants growing mostly at the bottom of the slope
Surface is Tilled - No soil moisture - See Section 4.3.6
Stones and Pebbles show clearly on surface - Erosion of Seeds etc. to Lower Slopes - See Section 4.2
Patchy Growth
Gas Smell and/or Stunted Brown Leaves - Landfill Gas Emission - See Section 4.5
Leachate or Stains Visible - Leachate Seep - See Section 4.4
Barren Areas
Evidence of Erosion
Stones and Pebbles exposed on surface - Sheet Erosion - See Section 4.2, 4.3.1
Rill Development - Rill Erosion - See Section 4.2
Gully Development - Gully Erosion - See Section 4.2
No evidence of Erosion
Cracked Surface (Clay) - Lack of Moisture - See Section 4.3.6
Small Sand Dunes (Sand) - Lack of Moisture - See Section 4.3.6
Not Previously Planted or Seeded - See Section 6.2

FIGURE 2: KEY TO PROBLEM IDENTIFICATION

- gas emissions; and
- poor or inappropriate existing vegetative cover.

Guidance is provided for undertaking some of the tests needed to evaluate the physical characteristics. In some cases, the manual specifies that the MOE be called for assistance, particularly where leachate and gas are involved, or if there are issues related to the Certificate of Approval.

c) Planning a program

Besides the obvious aesthetic requirement of revegetating a landfill site, a number of objectives were identified which should be satisfied by the vegetative cover. These are:

- to provide sufficient density of cover to reduce soil loss by rainfall impact;
- to provide sufficient density of shallow roots to bind the soil, especially at the surface, to resist the eroding forces of overland flowing water, and the cracking action of both the freeze–thaw cycle and the wet–dry cycle;
- to provide resistance or drag to flowing water and thus reduce its velocity and erosivity;
- to be self–sustaining, requiring low maintenance, with no root penetration of the cap; and
- to be capable of withstanding the intended end use.

In order to achieve these objectives, the characteristics of an ideal vegetative cover were identified:

- easy to establish, with good growth in the first growing season;
- sod forming with shallow, fibrous roots and multiple stem growth habit;
- self propagating by seeding, by root suckers, and/or perennial life cycle;
- low nutritional demands, tolerant of pH variation, ability to fix nitrogen, adaptable to variations in physical habitat; and
- reasonable tolerance to climatic extremes, especially drought tolerance.

Because of the great differences in climate and growing conditions in Ontario, the manual could not provide one recommended species or mix of species. Instead, the reader is provided with an understanding of how the ideal characteristics can be assembled from species which individually contribute to, and collectively satisfy the required cover characteristics, and are locally adapted and commercially available.

d) Implementation

A revegetation program is described, giving the landfill operator the correct sequence and timing of steps to be undertaken. These include the site inventory, soil testing, and the use and benefits of soil amendments, such as mulches, sewage sludge, lime and fertilizer. Guidelines on tillage, incorporation of soil amendments, and seeding techniques are provided. Approximate start–up and cut–off dates are provided for seeding in Northern, Southern, and Southwestern Ontario, with the best results usually obtained with spring seeding.

Instructions are given on how to obtain specialized supplies and seeds, soil tests, and professional and/or agency assistance.

e) Follow-up

The revegetation program may have involved a considerable expenditure of funds and resources. In order to obtain the maximum return from this expense, a commitment to follow-up care is essential. Appropriate recommendations are provided on:

- vegetation monitoring;
- soils monitoring;
- maintenance;
- keeping records; and
- getting professional and/or technical assistance.

V Conclusion

This manual provides two methods of assessing site characteristics, with explanations of site factors, why they can be a problem, and how they can be improved. The manual does not provide cook-book solutions: each landfill site has unique physical characteristics related to it. Rather, this manual provides a means of assessing problems and determining possible causes. Upon this basis, improvements can be planned and implemented, as required, in order to establish an appropriate vegetative cover. The key points to include in a maintenance program are identified. Sources of assistance, materials, and information are provided to facilitate the implementation of a revegetation program on a particular site.

VI Acknowledgements

We wish to thank the Ontario Ministry of the Environment for funding this project. We are grateful for the help and technical assistance provided by the MOE members of the project steering committee, and by the staff of the Regional and District Offices of the MOE. A special thanks goes to the owners and operators of the many landfills which were visited.

C3

QUANTIFICATION OF INFILTRATION THROUGH LANDFILL COVERS

by:

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1.0 INTRODUCTION AND BACKGROUND

Decommissioned municipal solid waste sites often rely exclusively on the use of an earthen cap to restrict precipitation access to the underlying refuse material. While some infiltration is desirable for sustaining vegetative growth on the site, excess infiltration water which percolates beyond the soil storage zone and enters the buried waste can accumulate in the landfill, leach wastes into groundwater and enhance landfill subsidence. Consequently, the successful performance of the entire landfill can be very much a function of interactive processes operating to control water balance within the landfill cover (Nyhan, J.W., T.E. Hakonson and B.J. Drennon, 1990).

To provide a direct measurement of that portion of the infiltration water which passes through a landfill cap, it has been proposed that a field-scale lysimeter be installed in the landfill of concern. Previous studies have been undertaken to evaluate prototypes of an economical field-scale lysimeter suited to installation in a landfill cover (Ecologistics, 1990). The lysimeters installed and monitored in this study are a slightly modified version of the previously studied prototypes. The terms of the contract required the installation of a set of three (3) lysimeters under each of two (2) decommissioned landfill sites. The two landfill sites were to differ with respect to the textural characteristics of the final cover material applied. Once installed, a monthly volumetric measurement was to be made of the through-cover infiltration collected by each lysimeter. Trends in the rate of infiltration within the year were also to be collected. A set of in-field infiltration simulation experiments were to be undertaken to verify the satisfactory operation of the lysimeter. Finally, a mathematical simulation was to be performed to compare the results of existing soil water movement models with the measured values. This paper presents the interim findings of this study, which was still in progress at the time of writing.

2.0 DESCRIPTION OF LYSIMETERS

The lysimeters, based on the Kohnke, Dreibelbis and Davidson (1940) classification of lysimeters, can be described as filled-in lysimeters according to the principles used in their construction. They can also be described as free-drainage lysimeters, given that they drain freely to the atmosphere by accumulating infiltration water in a storage chamber below the soil mass. A cross-sectional representation of the lysimeters installed on both the Guelph and Barrie landfills is presented in Figure 1. The Guelph and Barrie site of significant features associated with the lysimeters include the use of 40 mil PVC liner to form the lysimeter walls, the use of 600 mm (24") Big "O" heavy duty perforated pipe to form the storage zone, the cutting of vertical slots in the monitoring well within the lysimeter's storage zone and the installation of the mastic and bentonite skirt at points susceptible to preferential flow.

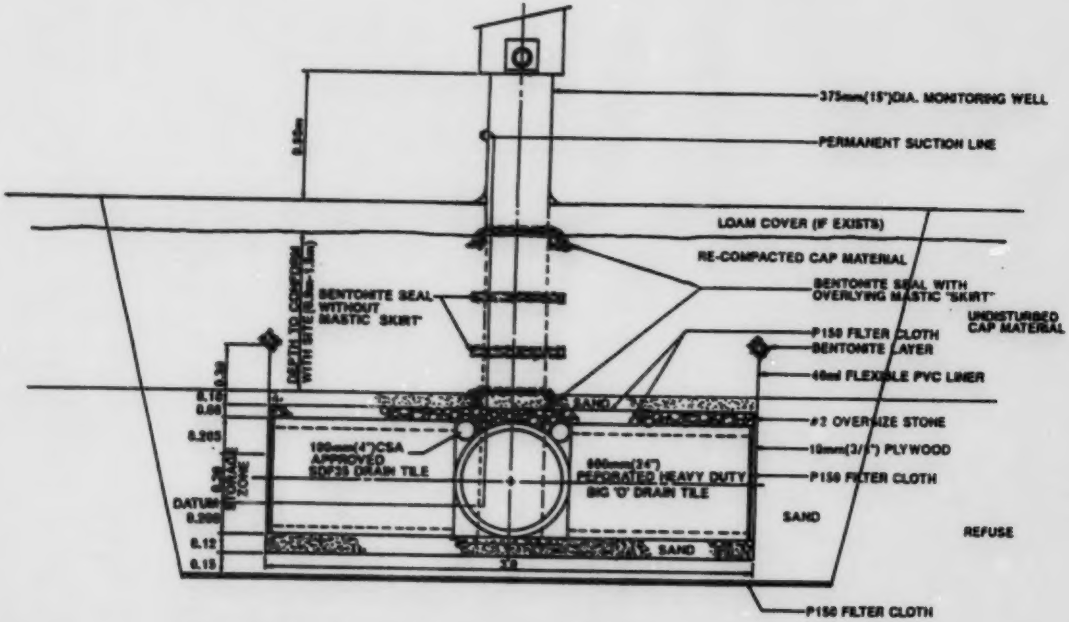
The use of large diameter pipe in the storage zone provides ample storage capacity and facilitates the incorporation of a flexible storage zone datum. Later it was also discovered that the heavy duty pipe is capable of withstanding heavy machinery traffic during cover installation.

The slots in the monitoring well ensures rapid gas and water exchange between the monitoring well and the storage zone, simplifying the monthly task of pumping out the collected infiltration water.

3.0 DESCRIPTION OF INSTALLATION SITES

With logistical assistance received from the Ministry's assigned liaison officer, approval was obtained from the appropriate authorities to install the lysimeters on the Guelph and Barrie landfill sites. The Guelph site is located on the eastern outskirts of the city. A textural analysis revealed the Guelph cover to be a gravelly loam material (see Table 1). The cover was compacted during its installation. Measured densities associated with the completed cover ranged from 1.9 g/cm^3 to 2.4 g/cm^3. The Barrie site, located just west of the city off an access road that extends to Ferndale Avenue,

FIGURE 1: Lysimeter Cross-section


375mm(15")DIA. MONITORING WELL
PERMANENT SUCTION LINE
LOAM COVER (IF EXISTS)
RE-COMPACTED CAP MATERIAL
BENTONITE SEAL WITH OVERLYING MASTIC "SKIRT"
UNDISTURBED CAP MATERIAL
BENTONITE SEAL WITHOUT MASTIC "SKIRT"
DEPTH TO CONFORM WITH SITE
P150 FILTER CLOTH
BENTONITE LAYER
40mil FLEXIBLE PVC LINER
SAND
#2 OVERSIZE STONE
10mm(3/8") PLYWOOD
P150 FILTER CLOTH
100mm(4")CSA APPROVED SDF35 DRAIN TILE
600mm(24") PERFORATED HEAVY DUTY BIG 'O' DRAIN TILE
SAND
REFUSE
SAND
P150 FILTER CLOTH
0.30
0.15
0.06
0.205
STORAGE ZONE
DATUM
0.200
0.12
0.15

NOTE: DIMENSIONS ARE SHOWN IN m UNLESS INDICATED OTHERWISE.

uses locally available sand as the cover medium (see Table 1). Cover densities at Barrie are in the order of 1.8 g/cm^3.

TABLE 1: TEXTURAL ANALYSIS OF THE CAP MATERIAL AT THE STUDY SITES

SITE	GR	VCS	CS	MS	FS	VFS	SAND	SILT	CLAY	TEXTURAL CLASS
	----------% by weight----------									
Guelph	37	3.7	5.0	7.8	19.9	13.7	50.1	40.4	9.6	gravelly loam
Barrie	0	2.5	10.8	36.6	37.9	6.1	93.9	3.6	2.4	sand

Timing of the lysimeter installation at both sites was such that it corresponded to the application of the final cover layer. For Guelph, this meant that, while the landfill cap itself had been applied at the time of lysimeter installation, the final loam cover or topsoil to support vegetative growth had not been added. A similar situation existed for the Barrie site. While a shallow covering was over the area of concern at the time of lysimeter installation, the final cover complex was not complete. With portions of the cover at both sites being applied following lysimeter installation, and with the ability of the lysimeters to withstand heavy equipment traffic, an improved situation existed to help ensure that similar cap and cover characteristics would be present over the installed lysimeters as are present within the surrounding monolith.

4.0 LYSIMETER INSTALLATION

Installation of the lysimeters at both sites was undertaken in September 1989. A rigid protocol was followed during construction. Installation began by digging a 4 m x 4 m hole in the cap. Depth of the hole was dictated by the cover depth, for the lysimeters were installed in the zone of garbage at a depth which resulted in the side walls extending only 0.3 m (1') into the overlying cap. As the cap was excavated, densities of the cap were taken using a neutron density probe at 15 cm (6") intervals. These densities were used as a reference for restoring the cap as close as possible to its original condition when replacing the cap material over the lysimeter. All pertinent elevations associated with the lysimeters such as the elevation of the patio stone at the base of the well were noted and related to a known benchmark.

Water level recorders including the shelter boxes were posititioned over the monitoring well following lysimeter construction. As well, each lysimeter's storage zone was filled with water to test for leaks. No leaks were detected. The water was then pumped down to the pre-determined datum using a submersible pump attached to a metal stand. This stand, when set on the patio stone at the base of the monitoring well, positions the pump's intake at the storage zone's zero datum. The Guelph lysimeters were fully functional by December 1989, while the Barrie lysimeters were fully operational by January 1, 1990. The landfill covers themselves, however, were not complete. The final loam cover and seeding was completed at Guelph in April 1990. The bulk of the 5 foot deep sand cover over the installed lysimeter at Barrie was applied between November 1989 and June 1990. Final seeding has not been completed to date at Barrie.

5.0 MONITORING RESULTS

A comprehensive monitoring program has been implemented in an effort to fully assess lysimeter operation and accurately quantify the volumes of infiltration collected. At both sites, the through-cover infiltration water collected in the lysimeter storage zone is pumped out and measured volumetrically monthly. The same submersible pump and metal stand as was used in the initial establishment of the storage zone's datum is used to pump out the storage lysimeter to ensure a constant reference point throughout the study. Volumes pumped out to the end of August 1990 are presented graphically in Figures 2 and 3 for Guelph and Barrie respectively.

In addition to monthly volumetric measurements, the water level recorder, having a 32 day clock, records the water level within the storage zone. Its primary purpose is to identify trends in the relative timing or rate of accumulation of drainage water to the storage zone. Figures 4 and 5 present the recorded water level results. The data as presented has been adjusted to account for the porosity within the storage zone (95%) and to provide a continuous accumulative record of infiltration for the period. The y-axis scales on these graphs have been made identical to each other to visually assist in

FIGURE 2: MONTHLY VOLUMES OF PRECIPITATION AND THROUGH-COVER INFILTRATION - GUELPH LANDFILL

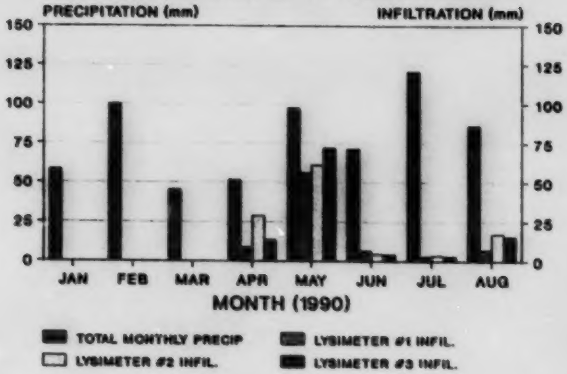


FIGURE 3: MONTHLY VOLUMES OF PRECIPITATION AND THROUGH-COVER INFILTRATION - BARRIE LANDFILL

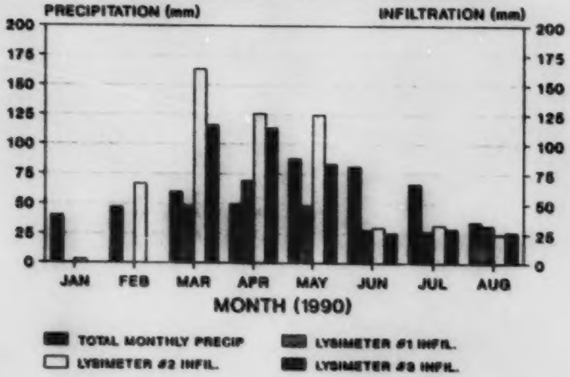


FIGURE 4
LYSIMETER MEASURED INFILTRATION
GUELPH SITE

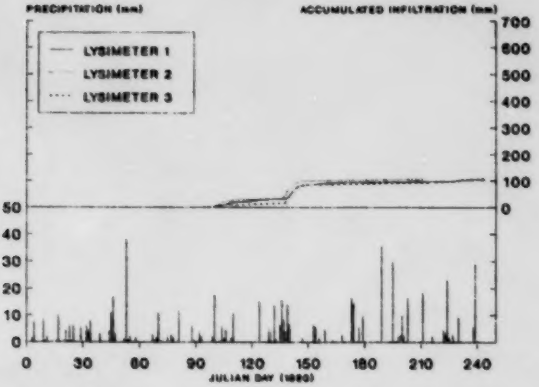
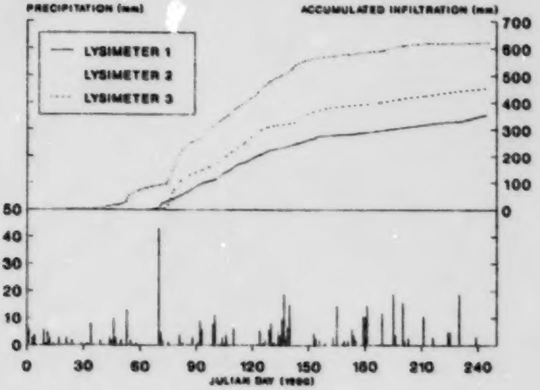


FIGURE 5
LYSIMETER MEASURED INFILTRATION
BARRIE SITE



comparing results between the Guelph and Barrie sites. Rainfall measured at a nearby weather station has also been added at the base of the graph to assist in identifying any possible relationships between precipitation and infiltration rates.

As seen from Figures 3 and 4, lysimeters at the Guelph landfill are giving nearly identical responses both in terms of infiltration volumes and the timing of infiltration. Barrie lysimeters show less similarity among each other. One main reason for this is the fact that the cover was still being applied on the Barrie site between January and June 1990. Consequently cover differences could easily have existed. Also, some of the cover was applied in the winter months when the opportunity existed for snow pack to be trapped in layers within the cover. This water would eventually drain during the spring thaw period. The graph in Figure 4 indicates that, while the Barrie lysimeters were collecting quite different levels of infiltration water until mid-April, trends since then have been quite similar. Time is required to see if this consistency among lysimeters continues now that the cover installation is complete.

Finally, note that to the end of August, infiltration levels through the Barrie cover have been on average 4.2 times higher, than for the same period at the Guelph site. Again, the delay in cover infiltration at the Barrie site is a factor here. If only data between May and August is considered, there is just a two-fold difference between the sites. The total infiltration measured at the Guelph site was on average 15% of the total precipitation that occurred in the same period. For Barrie, the average infiltration recorded was 73% of the total precipitation for the same period. Both sites are located on relatively flat areas of the landfill, encouraging water infiltration as opposed to water run-off.

Finally, a comparison was made between the direct volume measurements of infiltration and those indirect volume measurements made by converting changes in chart recorder readings to volumes. Field measurements and theoretical calculations have established the porosity of the lysimeter's storage zones to be approximately 95%. The surface area of the storage zone as constructed is known to be 3 m x 3 m. Chart recorder measurements are between 0.2% and 42% of the actual pumped values. This error is expected to originate to a certain extent from the inherent error associated with the chart recorders themselves which have a manufacturer's rated accuracy of ± 3 mm. In this application such an inherent error is the equivalent of 26 litres of infiltration water. Errors can also arise from the monthly disturbance which occurs during chart changing. Regardless of the source, such a range in error does emphasize the need to measure lysimeter infiltration volumetrically if monthly readings within 10% of the actual levels are desired. Such a procedure is relatively convenient.

6.0 FIELD SIMULATION

A field scale infiltration simulation experiment was conducted at both the Barrie and Guelph sites to further verify the reliability of the lysimeters as a through-cover infiltration measurement tool. The experiment entailed installing a water-proof barrier around the perimeter of a 4 m x 4 m area within which the lysimeter to be tested was located. A simple irrigation system was installed inside the barriers to apply water at a very slow rate. A flowmeter recorded the volumes applied over the 16 m^2 area. This same area was completely covered with plastic to minimize evaporation/transpiration losses. Initial application rates were estimated using the cover's infiltration and percolation rates as measured by the Guelph infiltrometer and permeameter respectively.

To establish a consistency in initial conditions for the experiments to follow, the soil profile was wetted up beyond saturation and allowed to drain to field capacity. Once field capacity was reached, known volumes of water were applied gradually to the enclosed area.

The soil profile was assumed to have reached field capacity at the point where the water level recording chart was showing a horizontal line with time. Three separate applications were performed. The volumes subsequently collected in the lysimeters were compared with the theoretical volumes expected assuming no evaporation/transpiration losses. Results of the three runs on the Guelph site are shown in Table 2. The Barrie experiments were underway at the time of writing. Consequently, results were not available for printing. The Guelph data, however, instills a high degree of confidence in the ability of the installed lysimeters to measure through-cover infiltration with an average of 94% of the expected infiltration being captured under saturated or near saturated initial conditions over the three trials.

TABLE [illegible] RESULTS OF FIELD SCALE INFILTRATION EXPERIMENTS - GUELPH SITE

EXPERIMENT	THEORETICAL VOLUMES OF INFILTRATION WATER AVAILABLE TO BE CAPTURED	ACTUAL VOLUME CAPTURED	PERCENTAGE OF THEORETICAL
A	170	168	99
B	170	152	89
C	170	161	95

7.0 COMPUTER SIMULATION

The Hydrologic Evaluation of Landfill Performance (HELP) model, developed by the U.S. Environmental Protection Agency was employed in this project's modelling task. Authors of the model describe the HELP model as follows:

> The (HELP) program was developed to facilitate rapid, economical estimation of the amounts of surface run-off, subsurface drainage, and leachate that may be expected to result from the operation of a wide variety of possible designs. The program models the effects of hydrologic processes including precipitation, surface storage, run-off, infiltration, percolation, evapotranspiration, soil moisture storage, and lateral drainage using a quasi-two-dimensional approach.
>
> (Schroeder, P.R., A.C. Gibson and M.D. Smolen, 1983)

While the HELP model is no more complex than a computerized form of a manual tabulation of moisture balance, it combines accepted state-of-the-art mathematical models for computing an accurate water budget over a variety of climatic, soil and vegetative conditions. The purpose of applying this computer model to simulate operation of the lysimeters was to determine the degree of accuracy with which the HELP model could predict through-cover infiltration amounts.

Climatic input to the model included the 1990 precipitation data measured at the weather station closest to the site under analysis and the average monthly temperatures for 1990. Given that little vegetative cover had established on the site in 1990, bare ground conditions were assumed. The landfill cover profile overlying the lysimeters was also described in detail to assist in infiltration modelling. Guelph permeameter percolation readings were taken at each site and used as an estimate of each cover layer's saturated hydraulic conductivity.

Graphed results of the HELP run at each site are presented in Figures 6 and 7. They have been prepared in a format similar to the graphs of Figures 4 and 5 to assist in comparing computer simulated results with lysimeter measured data. The simulation results did not resemble the field measured levels of through-cover infiltration. For the January through August 1990 period, the model estimated 2.3 times more infiltration than the lysimeters measured at the Guelph site, while it predicted 5.7 times less infiltration than what was measured at Barrie. The predicted timing or rate of through-cover infiltration was also different from that shown on the lysimeter's well level charts. Possible explanations for the differences are numerous. For example, it was not possible to model the gradual application of cover material over the Barrie lysimeters. In taking permeameter readings on the Guelph site, the stoniness of the cover material and the slow rate of infiltration made it difficult to set-up and conduct the permeameter tests. Further analysis needs to be completed to determine whether the model can be refined or calibrated in a manner which will produce more representative results.

8.0 CONCLUSIONS

While this study is still in progress, observations to date are directing the study team to the following conclusions.

1. The lysimeters as installed are giving true readings of volumes of infiltration water passing through the overlying cover material.

2. Monthly volumetric readings are necessary for accurate determination of the amount of through-cover infiltration water collected.

FIGURE 6
INFILTRATION SIMULATION - GUELPH SITE

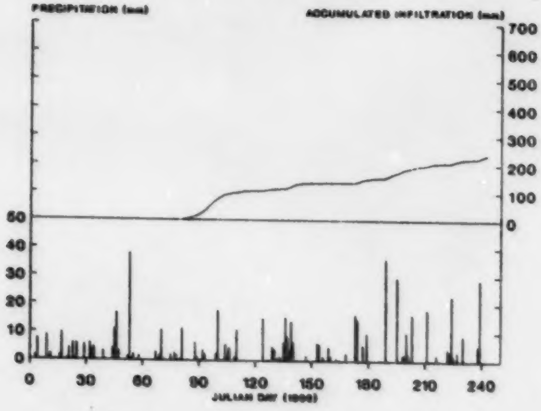
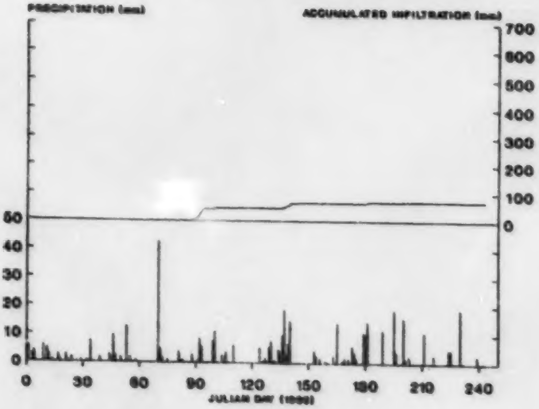


FIGURE 7
INFILTRATION SIMULATION - BARRIE SITE



3. The water level recorders can assist in identifying general trends with respect to the rate of through-cover infiltration within any given month.

4. Strict protocol must be followed during construction of the lysimeters to ensure proper installation and operation in the future.

5. Long-term monitoring of the installed lysimeters is necessary in order to assess the landfill cover's effectiveness in controlling through-cover infiltration.

6. Monthly monitoring of the lysimeters can be set-up to be a routine task.

7. The HELP model prediction of through-cover infiltration rates at both the Guelph and Barrie sites was poor. Refinements are needed for the model to produce desired results. Long-term data collected by installed lysimeters could provide data necessary to refine and calibrate an appropriate model.

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Accurate Control Testing for Clay Liner Permeability

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ABSTRACT

Experience with commercial testing of clay liner samples for permeability evaluation has shown that standard laboratory permeability tests are subject to leakage problems which can effect the order of magnitude of the results. Furthermore, these tests typically take a week or more to complete and are, therefore, inadequate as field control tests. Physical modelling of various geo-environmental problems in a geotechnical centrifuge was initiated at Queen's University, Civil Engineering Department, in 1988 and it became apparent that the behaviour of clay liners was one of the problems for which centrifuge modelling was well suited. A dedicted 0.5m radius centrifuge was constructed, principally for long term behavioural studies of clay liners but which could also be used for control testing. This paper outlines recent research on the use of the 0.5m radius centrifuge for accurate control testing for clay liner permeability.

The test results are presented in three phases. The first phase used commercial kaolin clay samples prepared by consolidation into a specially designed permeability apparatus. This apparatus was designed for both bench and centrifuge use and allowed a direct comparison of the two methods. The centrifuge method was found to be efficient and reliable. The second phase of this research used a highly impervious compacted clay liner material in the Queen's University 3m radius geotechnical centrifuge. A methodology for accurate clay liner control testing in the centrifuge was developed. The third phase of testing was carried out to examine some longer term permeability variations in compacted liners as a preliminary evaluation of the usefulness of the 0.5m radius centrifuge for liner performance modelling.

The results of this of this research shows that a geotechnical centrifuge can be used to provide accurate control testing for clay liner permeability. The 0.5m radius centrifuge is relatively inexpensive, sufficiently mobile for field operations and can provide a one day liner permeability results in most cases.

INTRODUCTION

A number of researchers and consultants have had experience with clay liner permeability testing in the laboratory and in the field and the general concensus appears to be that liner leakage testing is wrought with problems (see for examples, Chapuis (1990a), (1990b); Quigley (1990); Mitchell (1990).

Leakage errors in the testing apparatus and the long time required to obtain a satisfactory test result are the two major concerns in laboratory control testing. Field testing is not useful for hydraulic conductivities less than 10^{-9} m/s. A geotechnical centrifuge offers an alternative, relatively rapid and problem free method of evaluating clay liner leakage. A major problem with the specification of centrifuge models as a primary means of commercial liner permeability testing is the limited availability of geotechnical centrifuges. To alleviate this problem, the author has developed a 0.5m radius centrifuge for mobile testing. This paper presents the results of liner leakage testing carried out in this centrifuge.

The research is divided into three phases. Phase 1 research was conducted in the 0.5m radius centrifuge using a consolidated commercial white kaolin clay which was mixed at 100% water content (by dry weight) and consolidated into the permeability testing apparatus. The purpose of phase 1 research was to carry out a sufficient number of bench permeability and centrifuge permeability tests on saturated uniform clay to determine whether the two methods give similar results. Phase 2 research was carried out in the 3m radius centrifuge. The purpose of phase 2 research was to compare the results of triaxial permeability tests on a relatively impervious compacted clay to liner leakage model testing in a moderate sized geotechnical centrifuge. Phase 3 research used the same compacted clay at various moisture contents to carry out a preliminary evaluation of the 0.5m radius centrifuge for use in evaluation of the long term field performance of clay liners and was in progress at the time of writing of this paper.

A prototype clay liner will be overlain by landfill materials which may become saturated with liquids and, over a long period of time, liner leakage may occur. This worse case condition (or any other operational condition) can be modelled in a geotechnical centrifuge. Such centrifuges have been used world-wide for geotechnical physical model testing for the past two decades and are recently being used for research into other civil engineering problems, including environmental engineering problems. In its simplicity, the centrifuge simulates gravitational forces by induced centripetal forces so that a small model may experience prototype stresses and prototype flow and fracture phenomenon. The induced simulated gravity is given by

$$\lambda = r\omega^2/g \qquad (1)$$

where λ is the liner scale factor, r and ω are the centrifuge radius and speed, respectively, and g is the earth's gravitational constant. For a detailed review of geotechnical centrifuge applications, the reader is referred to Schofield (1980).

The total and effective stresses at all similar points in the model and prototype liners will be identical but the hydraulic gradient across the model liner will be increased by the modelling scale factor. If, for example, a prototype liner of 2m thickness is supporting an overlying 20m head of water, the hydraulic gradient is 10. If a model is designed at a scale factor of $\lambda = 35$, the 57mm thick model would then have an hydraulic gradient of 350 and one day of testing in the centrifuge at $\lambda = 35$ would produce λ^2 days or 3.35 years of prototype per unit area leakage. In fine grained soils Darcy's Law is considered to be applicable over a wide range of gradients (Goodings, 1985).

TEST METHODS

Most methods of measuring permeability of soils involve potential variations and errors. Variations develop in the preparation of most soil samples and errors result from equipment leakages. To carry out a meaningful statistical evaluation of the centrifuge method of clay liner permeability testing it was necessary to develop a leak-proof apparatus in which both bench and centrifuge permeability tests could be carried out under similar conditions on the same samples of a uniform and reproducable clay soil. A saturated consolidated commercial kaolin clay was selected, due to both uniformity and order of magnitude of permeability, as the most suitable clay material. Clay samples for bench permeability testing were preconsolidated to 250 kPa. During a test the sample is surrounded by a silicon rubber membrane and a silicon oil pressure seal of 100 kPa to prevent any possibility of leakage. The hydraulic head applied across the 50mm thick sample was 50 kPa, creating a nominal gradient of 102 and a seepage pressure of about 50 kPa. Over a three month test period a total of 16 independent tests were carried out.

The phase 1 samples remained in the permeability apparatus during transfer from bench to centrifuge and the boundary stress conditions were similar in each test. The centrifuge induced hydraulic gradient across the sample, however, is 163 and the seepage pressure is 80 kPa. Thus the flow rate in the centrifuge is about 1.6 times faster than in the bench test. Never-the-less, the test conditions in both methods are considered closely similar. The test time in the centrifuge was about 3 to 4 hours compared with 6 to 8 hours in the bench tests. The mass of water in the catchment container was measured after one hour of spinning and again at the end of the test. The one hour check point served the purpose of determining whether any consolidation or other "initial phenomenon" were taking place in the centrifuge. In most cases the N hour mass transfer was very close to N times the one hour mass transfer.

In order to compare centrifuge leakage models with triaxial permeability testing, phase 2 testing included double membrane, back pressured triaxial permeability tests on a local illite clay material. A standard Proctor compaction test on this clay gave a maximum dry density of 1.37 g/cc at an optimum water content of 35.5%. The material was stored at this water content and was subjected to standard Proctor compaction to form samples which were subsequently trimmed for permeability testing. After testing the used materials were remixed with the original batch and stored for further testing. Two triaxial cells with back pressured systems (Bishop & Henkel, 1962) were newly assembled, platens were polished and leakage testing of the systems was carried out before the permeability testing was begun. In total, six acceptable tests were carried out over a two month period. This is an average of less than two tests per cell-month, mainly because the system required considerable attention and repair during that time period.

The Queen's 3m radius centrifuge is described by Mitchell (1986) and Figure 1 shows the apparatus developed for liner modelling. The liner model is nominally 50mm thick, and is trimmed to fit snuggly in a double thickness membrane encased perspex ring. The overlying landfill materials are simulated by a known mass of lead shot overlying a porous plastic disk placed on the top of the liner model. Double thickness filter paper and a porous stone underly the model. Stand pipe arrangements are used to create the water pressure and the confining pressure, which both increase as the simulated gravitational force increases in flight. The confining pressure is maintained at 35 kPa above the water pressure in order to effect a tight contact between the liner model and the rubber membrane. Phase 2 testing was carried out at a scale factor of λ = 35 with the model representing a 1.7m thick prototype liner. The centrifuge induced hydraulic gradient was 420.

TEST RESULTS

The phase 1 test data is summarized on Table 1. It can be noted that the earliest samples, KP 1 to 4 showed relatively high permeabilities because the preconsolidation pressure was below the desired level of 250 kPa. These samples also gave apparent permeabilities from the centrifuge method which are 1.3 to 1.8 times higher than in the bench test. This is due, no doubt, to consolidation under the simulated gravitational stresses induced in the centrifuge. In this case the effective vertical stress is given by

$$\sigma_v^1 = (z\rho\lambda + iz\,\rho\omega)g \qquad (2)$$

where z is the sample thickness, g is the gravitational constant, ρ is the sample density, λ is the scale factor (a/g), i is the induced hydraulic gradient and $\rho\omega$ is the density of water

The value of σ_v^1 in the centrifuge model is then calculated to be about 120 kPa. The applied confining stress in the early test was 80 kPa and this would also have contributed to sample consolidation. Subsequent samples were all consolidated to a vertical effective stress, σ_v^1, of 250 kPa and a confining stress of 100 kPa was used in subsequent tests. It can be seen from Table 1 that subsequent tests (samples KP5 to KP16) provided a fairly consistent set of permeability data. All test data was plotted to obtain the best fit slope of the volume change vs. time line from which the permeability was calculted. The data on Table 1 clearly shows that the 0.5m centrifuge can be used effectively and efficiently to evaluate the permeability coefficient (hydraulic conductivity) of a consolidated clay material.

The results of the phase 2 triaxial permeability testing are contained in Table 2. All samples for which results are tabulated were back pressured to 300 kPa and subjected to an hydraulic gradient of 40. This laboratory testing was carried out at 20°C. From the data it is estimated that the mean permeability value is close to 2.3×10^{-11} m/s with individual test values from 0.3 to 1.3 times the average value. For material evaluation, this data seems reasonably acceptable although the scatter is quite significant.

Phase 2 liner leakage model tests were carried out over periods varying from five hours to ten hours. During some tests the centrifuge was stopped every two hours to check the mass transfer of water by weighing the catchment container (±0.005 g). Mass transfer quantities were in the order of 0.1 g/hr and the variance found during the two hour interval tests was generally less than 20%. Table 3 shows the data from all of the centrifuge liner leakage model tests carried out. The average leakage rate, from the data on Table 3, is 0.10 cc/hr with a maximum individual test variance of 20% The water temperature in the centrifuge liner model apparatus increased 0.5°C above the constant laboratory temperatures of 20°C during the first hour or two of spinning at 108 RPM and then remained constant throughout the remainder of the test. The calculated coefficient of permeability, from the average leakage rate is 2.2×10^{-11} m/s. With standard temperature correction, the hydraulic conductivity is estimated to be 2.0×10^{-11} m/s. This value is remarkably close to the average obtained from the triaxial permeability testing but the centrifuge data is more consistent than the triaxial data. This provides some confidence in individual liner control tests carried out by centrifuge modelling.

The compacted liner samples used in phase 2 are more dense than the consolidated samples of phase 1 such that there would be no consolidation during centrifuge liner leakage model tests on compacted samples.

CONCLUSIONS AND RECOMMENDATIONS

From the test data reported, it is concluded the centrifuge model liner leakage testing gives more consistent results for a low permeability compacted soil than triaxial permeability testing. The latter testing is subject to both technical difficulties and leakage risks. It is concluded that a centrifuge liner leakage model can provide realistic liner performance evaluation and that the hydraulic conductivity obtained from such a model will be closely similar to the average values found from good quality triaxial permeability testing.

The main advantages of centrifuge liner leakage models over any permeability tests are:
(1) Realistic modelling of stress conditions in the liner.
(2) Elimination of leakage provides more consistent results.
(3) Elimination of induced hydraulic fracturing.
(4) Rapid evaluation for construction control testing.
(5) Greater potential for modelling liner performance.

A complete specification for accurate control testing for clay liner permeability using the 0.5m radius centrifuge has been prepared. This machine is relatively inexpensive and provides a one day control test result in most cases. It is recommended that the centrifuge method of liner leakage control testing be approved for use on liner clay liner construction projects. Further research on liner performance modelling is also recommended.

ACKNOWLEDGEMENTS

Phase 1 and Phase 3 tests, as reported herein, were carried out with the financial support of an Ontario Ministry of the Environment contract (Project 506C). The Author also acknowledges the support of the Natural Sciences and Engineering Research Council of Canada for financial support of centrifuge modelling and, in particular, support for the phase 2 testing program.

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		BENCH TEST		CENTRIFUGE TEST	
Sample No	Saturated density g/cc	test time min.	hydraulic conductivity m/s x 10^{-9}	test time min.	hydraulic conductivity m/s x 10^{-9}
KP1	1.82	450	1.46	180	2.65
KP2	1.81	450	1.65	180	3.05
KP3	1.84	810	1.10	210	1.58
KP4	1.88	810	1.35	210	1.73
KP5	1.91	480	1.12	240	1.13
KP6	1.90	480	1.05	240	1.14
KP7	1.95	420	0.96	180	1.06
KP8	1.87	420	1.27	180	1.27
KP9	1.90	420	1.27	180	1.37
KP10	1.86	420	1.18	180	1.19
KP11	1.87	450	1.21	240	1.30
KP12	1.92	450	1.10	240	1.21
KP13	1.88	1100	1.28	180	1.23
KP14	1.94	1100	1.11	180	1.12
KP15	1.86	465	1.15	180	1.24
KP16	1.89	465	1.15	180	1.11

Table 1 - Phase 1 Test Results Summary

Test No	Test Time (days)	hydraulic conductivity m/s X 10^{-11}
LPTX2	9	3.3
LPTX3	8	0.8
LPTX4	7	0.9
LPTX5	8	5.3
LPTX6	12	1.1

Table 2 - Phase 2 Triaxial Tests

Model No	Run time (hrs)	Hydraulic conductivity (m/s X 10^{-11})
LPCM1	5	2.0
LPCM2	7	2.2
LPCM3	8	2.2
LPCM4	6	2.6
LPCM5	10	1.8
LPCM6	8	2.5

Table 3 - Phase 2 Centrifuge Models

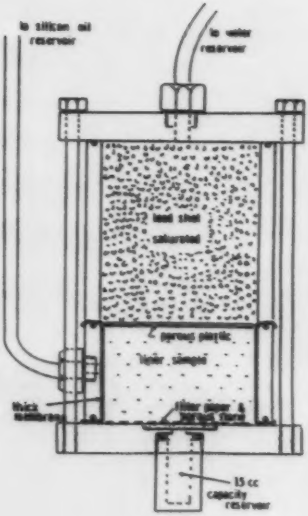
to silicon oil reservoir
to water reservoir
lead shot
saturated
porous plastic
liner sample
thick membrane
filter paper & porous stone
15 cc capacity reservoir

Figure 1 - Drawing of the Centrifuge Liner Model Apparatus

Field Demonstration of Membrane Technology for Treatment of Landfill Leachate

by

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Abstract

Landfill leachates commonly contain a wide spectrum of organic and inorganic contaminants which may pose a threat to surface or groundwater use. A variety of treatment processes have been considered and evaluated for the treatment of landfill leachates, including both biological and physical/chemical treatment processes. The objective of this study was to provide a technical and economic assessment of a membrane based process for treatment of landfill leachate. A two-stage process incorporating precipitation/microfiltration to remove heavy metals and suspended solids, followed by reverse osmosis to remove residual organics and dissolved metals was developed and tested by Zenon at pilot scale for treatment of a low strength landfill leachate.

Results of the field testing program demonstrated that the microfiltration system achieved stable flux rates ranging from 92 to 132 litres/meter^2/hr. A reverse osmosis system was used to further treat the MF permeate, and stable fluxes of approximately 32 litres/meter^2/hr were obtained with the RO. Overall process removals for key contaminants of concern were generally over 90%, at waste volume reductions of 75-80%.

A comparison of the costs of the developed process with alternative conventional processes was conducted and indicated that a treatment process incorporating conventional precipitation/clarification and reverse osmosis can provide a cost effective alternative to biological treatment at some sites, and may be particularly suitable for application where treatment is required prior to spray irrigation or recirculation. In order to further evaluate potential applications of this technology, a pilot scale testing program should be undertaken to determine the performance and cost of membrane treatment for higher strength landfill leachates.

Introduction and Background

Landfill leachates are complex wastes containing a variety of both organic and inorganic contaminants. The quality of leachate varies substantially between sites, and is affected by the type of waste disposed, site specific hydrogeology, age of the landfill, and the biodegradability of the different organic contaminants present. As a result, a variety of treatment processes have been considered and evaluated for treatment of landfill leachate. Biological treatment has been used reliably and effectively however, leachates which have a larger proportion of higher molecular weight refractory organic contaminants, or high levels of toxic metals, may not be readily amenable to biological treatment. Research undertaken over the last few years has demonstrated the technical feasibility of reverse osmosis and other membrane processes in various capacities for the treatment of industrial wastes, and recently, for application in the treatment of landfill leachate.

Membrane Separation

Membrane based systems hold significant potential for treatment of such leachates and may be incorporated with other pre and post- treatment processes, including biological or physical/ chemical treatment, as appropriate. Membrane separation is referred to as a cross-flow filtration process since the flow of feed is across the membrane surface. The three main membrane filtration processes (microfiltration, ultrafiltration and reverse osmosis) are all based upon flow through a semi-permeable membrane where pressure is the driving force, however they each have different membrane characteristics, separation principles, and operating conditions.

In the microfiltration process, the filtration surface is a strong polymeric membrane cast on the inside surface of a support tube, as shown in Figure 1. Feed is pumped at relatively low pressures (up to 60 psi) through the membrane tube. The water and dissolved components pass through the membrane as clean filtrate or permeate, while suspended solids and fine particulate material are retained by the membrane and remain with the feed. The feed becomes more concentrated as it flows down the membrane tube. Turbulence from the flow keeps the filtration surface clear of any build up of contaminants which would reduce the filtration or permeate rate. Microfiltration (MF) processes have pore diameters of 0.08 to 1.0 microns, and effectively remove suspended solids which are not easily settled. MF has been applied to the treatment of contaminated wastewaters as the solids removal step after chemical precipitation of toxic metals.

Ultrafiltration processes (UF) operate in a smaller filtration range, with pore diameters of 0.002 to 0.1 microns, and are commonly used for the concentration of wastewater containing emulsified oils or large molecular weight organic contaminants.

Finally, reverse osmosis (RO) processes have a filtration range of less than 0.002 microns and are used for the removal of dissolved solids (salts) and dissolved organic contaminants. In reverse osmosis the contaminated water is passed under pressures from 200 to 1,000 psi across a membrane surface. Pure water preferentially permeates the membrane, leaving the suspended and dissolved contaminants concentrated on the feed side. Rejection levels are depended on the size and charge of the dissolved molecule with larger molecules and higher charge being more highly rejected.

Process Development

In 1988, bench scale work was undertaken by Zenon on behalf of the Ontario Ministry of the Environment to evaluate the potential for reverse osmosis as part of a complete system for the treatment of landfill leachate. Results of the bench scale study confirmed the technical feasibility of the two stage membrane-based process (Krug and McDougall, 1988).

Figure 2 presents a schematic of the process developed. The first stage involves pH adjustment and precipitation of heavy metals and hardness, followed by microfiltration. The potential benefits of the process over conventional precipitation and settling processes include the ability of the process to completely remove toxic heavy metals, and remain insensitive to upset conditions and sludge settling characteristics. A membrane process is also compact in size relative to conventional clarifiers. The resulting primarily inorganic sludge, generated as concentrate from the MF, would be dewatered in a plate and frame filter press and the filter cake disposed appropriately.

The MF permeate containing dissolved organics and inorganics would then be subjected to final polishing by reverse osmosis to produce a high quality effluent. Reverse osmosis will serve to reduce hydraulic loading on any downstream treatment processes such as spray irrigation, reduce volume for off-site disposal, and generate a high quality product stream suitable for surface discharge. The concentrate from the RO process, containing primarily organic components which were not removed in the first stage precipitation/microfiltration process, can be disposed of off site, used for spray irrigation, or recycled to the landfill site itself.

This process was recently tested at pilot scale at a landfill site in Ontario. The objectives of the field program were to continue the development of a membrane based process for treatment of landfill leachate by conducting a pilot scale field demonstration, and to provide an assessment of the technical effectiveness and cost of the process based on pilot scale data.

Field Testing Program

Site Description

The Muskoka Lakes Sanitary Landfill site was selected for pilot scale evaluation based on leachate quality and quantity, treatment requirements, as well as site access and availability of support services.

The leachate at the site is presently collected in a trench which is situated downslope of the site. It is collected in a sump, pumped to two settling lagoons where a limited degree of natural aeration and biodegradation occurs, and then pumped to a network of spray nozzles for land distribution over a forested area. The volume of leachate requiring treatment is expected to exceed the capacity of the current spray irrigation system and researchers have found that pretreatment is necessary to prevent damage to vegetation (McBride et. al., 1988). A process capable of reducing both chemical concentration and hydraulic loading would therefore be of benefit at such sites.

The primary contaminants of concern in this leachate are Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), iron, manganese and solids. The leachate was relatively dilute, with TOC and BOD levels at approximately 250 mg/L, COD at 580 mg/L, and Iron at 150 mg/L. Key volatile organic contaminants are shown to be toluene, with low levels of benzene and ethylbenzene. Low levels of several chlorinated solvents were also detected, including 1,1-dichloroethane, and 1,2-dichloroethane.

System Design

The pilot scale treatment system was designed with the objective of maximizing performance and effluent quality, in order to generate an effluent suitable for surface discharge.

The microfiltration test unit consisted of a polyethylene tank, a single stage centrifugal pump, two tubular membrane test modules (operated in parallel), a central control panel, a clean-in-place tank, and associated tubing, valves and pressure gauges. The total feed flow rate was 40 gpm, operated at 60 psi. The membranes used for the field testing program were Zenon AST membranes, which have a neutral charge and a molecular weight cut off of approximately 200,000. The microfiltration membrane module contains eight tubes in an internal series flow configuration. Each tube is 2.1 cm (0.84") in diameter and approximately 1,956 cm (77") in length, for a total surface area per module of 0.98 m^2 (10.5 ft^2). The high turbulence in the large diameter membrane tubes allows the membranes to tolerate high levels of suspended solids and maintain consistently high permeate rates.

The MF permeate was then fed into the RO system. The reverse osmosis test system consisted of a 650 L polyethylene tank, a feed pump, a process pump, one 4" X 40" Filmtec FT 30 spiral membrane module, a central control panel, a clean-in-place tank, interconnecting piping, valves and pressure gauges. The feed was pumped at a rate of 5 gpm at 400 psig.

Results and Discussion

The microfiltration/reverse osmosis pilot system was installed on-site in September, 1989, and performance was evaluated through a series of twelve tests over an eight week period.

Reverse osmosis treatment processes generally require pretreatment to remove particles larger than 5 µm, and to remove and feed components which could potentially foul, damage or scale the membrane units. The impact of complex wastes on membrane performance is difficult to predict and must usually be determined based on laboratory and/or field testing. Prior to the field program, a short series of bench scale tests were conducted to confirm the pretreatment requirements. Suspended solids, iron and calcium salts can foul RO membranes, thus chemical precipitation is required prior to the microfiltration step to reduce the concentration of the contaminants in the MF permeate. Both sodium hydroxide and lime were evaluated to precipitate metals, and lime precipitation was selected for the field trials based on superior membrane flux.

The pilot system was designed and operated in a batch treatment mode. Stability tests were initially conducted to establish baseline fluxes upon exposure to the feed. A series of concentration tests were then conducted to establish performance at various concentration factors. Since volume reduction was limited by batch size due to tank and pump configuration, several tests were conducted to treat a larger batch and thereby more closely simulate continuous operation. This was achieved by reducing the feed volume to a desired concentration level, and then adding fresh feed to top up the tank. Chemical dosages were also optimized during the study. The final two runs were conducted under optimized treatment conditions and represent the best performance achieved during the study.

Microfiltration Performance

The permeate rate, or flux, and the extent to which the feed can be concentrated without fouling the membrane, are important performance criteria. The microfiltration tests demonstrated that high and stable flux rates, ranging from 92 to 123 litres/cubic meter/hour (LMH), can be maintained using raw leachate treated with lime, even at volume reductions greater than 90%.This represents a concentration factor of ten, since 90% of the volume in the feed was recovered as treated permeate. Figure 3 presents the flux, or permeate rate, obtained during the course of one of the final optimized runs. The operating conditions of volume reduction and operating temperature are presented to show how the permeate rates were affected by these variables. In this run, lime was added to raise the pH of the feed from approximately 6 to 8. As expected, the flux was affected by operating temperature but the effect of increasing volume reduction was generally quite small.

The results of chemical analyses for the final optimization test are given in Table 1. In general, the results confirmed that all suspended solids and metals were effectively removed by the MF. Solids and metals, specifically iron, were removed to at or near detection limits. The consistent removal of iron is important for downstream RO operation. Calcium, which was contributed mostly by the lime used to raise pH was reduced by approximately 70%. As expected, very limited reduction in organics was observed since most organic contaminants would be small enough to pass through the MF membrane.

The permeate, having no suspended matter and containing only dissolved organics and inorganics was suitable for further polishing by RO.

Reverse Osmosis Performance

The pH of the MF permeate was adjusted to approximately 6 by the addition of HCl to reduce the potential for calcium carbonate scale formation during reverse osmosis concentration. Figure 4 presents the permeate rates obtained during the final optimization run. Rates were stable at approximately 32 LMH at volume reductions over 80%. However, at concentration levels over 75% , soda ash must be used along with the lime prior to MF in order to further reduce tendency for scale formation in the RO system.

Analytical data are presented in Table 1, along with overall process rejections. The results confirm that the RO process is capable of removing a very high percentage of the organics present. Values for TOC were reduced from an average of 200 mg/L by 94% down to an average of 12 mg/L. Values for BOD were reduced from an average of 230 mg/L by 93% down to 14 - 15 mg/L. This high quality of RO treated water satisfies the general surface discharge guideline of 25 mg/L BOD. Toluene which was present at approximately 120 µg/l in the raw feed was reduced by about 50% across the MF, with a further reduction down to 14 µg/L across the RO. Total dissolved solids were reduced from 600 mg/L to about 130 mg/L in the final effluent.

The RO permeate met most criteria for surface water quality, as well as key drinking water quality parameters, and would therefore likely be suitable for surface discharge.

Economic Assessment

The field test results confirmed that the process was technically effective. An economic assessment was then carried out in an attempt to estimate the cost of a membrane based process compared with other process trains capable of achieving similar effluent quality. Capital and operating costs were developed for each of three different treatment process, with capacities ranging from 55 to 165 m^3/day. Equipment costs are based on manufacturers selling price for packaged skid-mounted system components. The installed costs include all costs associated with the facilities including foundations, instruments, piping, insulation, buildings, and services, as well as construction and field expenses, engineering and contractors fees. For the purpose of this cost comparison it has been assumed that the dewatered solids generated from both the precipitation/MF and precipitation/clarification processes can be disposed at the landfill site at a nominal cost.

The processes considered in the economic assessment are as follows:

1) precipitation/MF for metals removal followed by reverse osmosis to reduce the volume of leachate water, and irrigation of the concentrated organic stream for final disposal on-site

2) precipitation/clarification and sand filtration for metals removal followed by RO and irrigation on-site

3) precipitation/clarification and sand filtration for metals removal followed by rotating biological contactor to degrade the organic contaminants present.

Processes 1 and 2 above are based on the assumption that the organic concentrate can be disposed of by spray irrigation or other means at the landfill site. If on-site disposal is not feasible, the cost of hauling or disposal of residue would be added to the the first two processes, and would be dependent on distances and associated disposal costs.

The capital and operating cost comparison of the three treatment trains indicated that the cost for the treatment process tested during the field evaluation (Process 1) was the highest of the three alternatives considered, at $4.66 per thousand liters for a system capable of treating 165 m^3/day. This is mainly due to the fact that costs for the precipitation/MF process, which are based on fluxes achieved during the test runs, proved to be somewhat higher than for conventional precipitation/clarification for removal of metals and suspended solids. The cost-competitiveness of the MF process could be improved if the capacity performance or flux of the membranes can be improved, if the cost for the membranes can be reduced or, if non cost issues, such as assured removal of all suspended solids or limited site space dominate the evaluation.

Process 2, where conventional precipitation/ clarification is used as the metals removal step and reverse osmosis is used for organics removal, was the least expensive option, at $3.23 per thousand liters.

Process 3 was based on conventional precipitation clarification followed by a Rotating Biological Contactor for degradation of organics was estimated to cost approximately $3.68 per thousand liters.

Conclusions and Recommendations

The results of the field testing program indicated that the precipitation/microfiltration and reverse osmosis process was successful in achieving surface water quality and drinking water quality objectives for all inorganic parameters of concern. Organic parameters were at or near drinking water quality guidelines.

The first stage precipitation/microfiltration process was capable of effectively removing suspended solids and metals from the raw leachate. The permeate contained only dissolved organics and inorganics and was suitable for further polishing by RO. The second stage reverse osmosis system was successful in removing a high percentage of the organic contaminants present as TOC, COD, and BOD, as well as dissolved solids, from the MF permeate. The RO was capable of achieving 80% volume reduction, and generated a high quality final process effluent and a concentrated, primarily organic residue.

A cost comparison of three alternative treatment trains indicated that conventional precipitation/clarification was less expensive than precipitation/microfiltration as a form of pretreatment prior to RO for this application. The costs of a treatment process using conventional precipitation/clarification for metals removal followed by reverse osmosis compare favourably with the costs for precipitation followed by biological treatment in the form of an RBC, where organic concentrate can be disposed on site. The process may be particularly suitable for application at sites where recirculation or spray irrigation practices are limited by excessive hydraulic loading or toxic metals. This option may also have an advantage over biological treatment in applications where immediate start-up of a treatment process is required because it does not require establishment of an acclimated microbial population. Further testing of this process at larger scale should be undertaken to evaluate performance and treatment costs on higher strength landfill leachates.

Acknowledgement

The authors wish to acknowledge the assistance of the Ontario Ministry of the Environment, who provided funding and technical support for this study (RAC Project 439C).

References

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McBride, R.A., Gordon, A. M. and Groenevelt, P.H., 1988. "Treatment of Landfill Leachate by Spray Irrigation (Muskoka Lakes), Ontario Ministry of the Environment, Research Advisory Committee, Project No. 244-RR.

Figure 1

Cross Flow Filtration

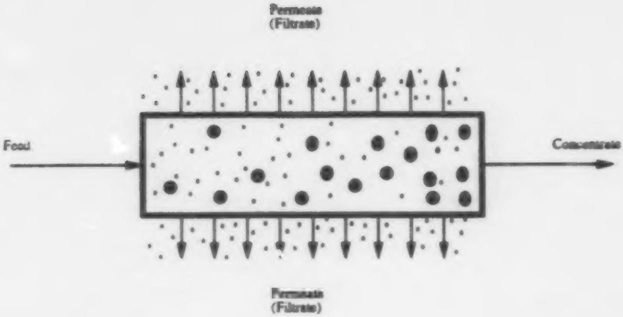
Permeate
(Filtrate)
Feed
Concentrate
Permeate
(Filtrate)

Figure 2

Process Schematic for
Treatment of Landfill Leachate

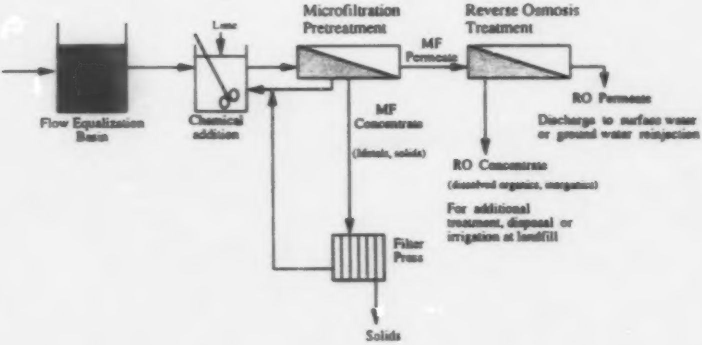
Microfiltration
Pretreatment
Reverse Osmosis
Treatment
Lime
MF
Permeate
Flow Equalization
Basin
Chemical
addition
MF
Concentrate
(Metals, solids)
RO Permeate
Discharge to surface water
or ground water reinjection
RO Concentrate
(dissolved organics, inorganics)
For additional
treatment, disposal or
irrigation at landfill
Filter
Press
Solids

Figure 3

Microfiltration System Operation - Pilot Test # 11

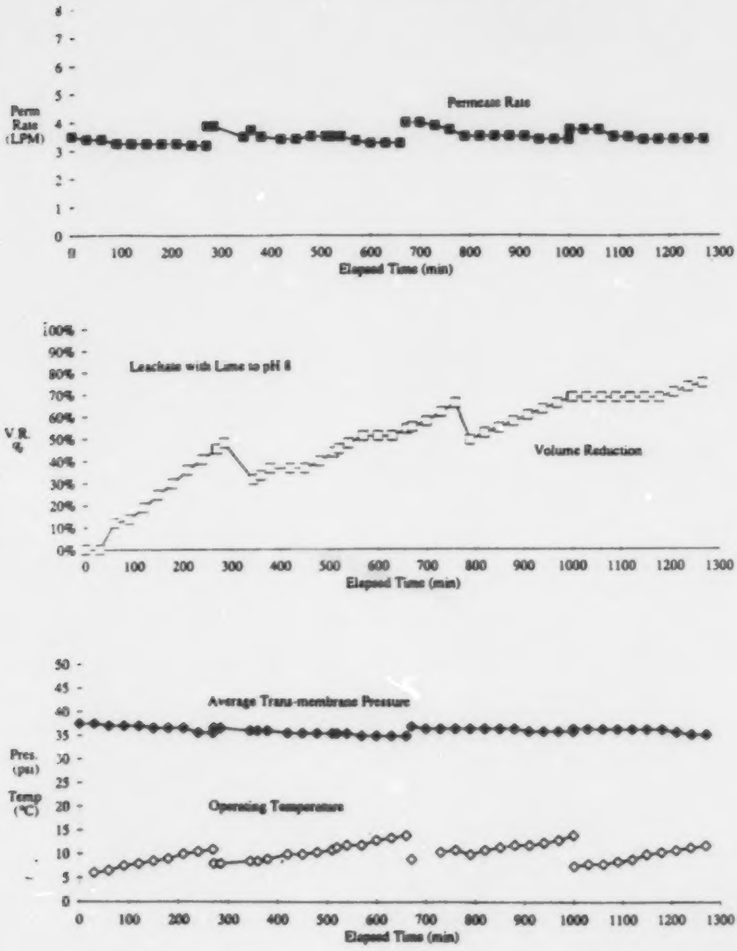

Figure 4

Reverse Osmosis System Operation - Pilot Test #12

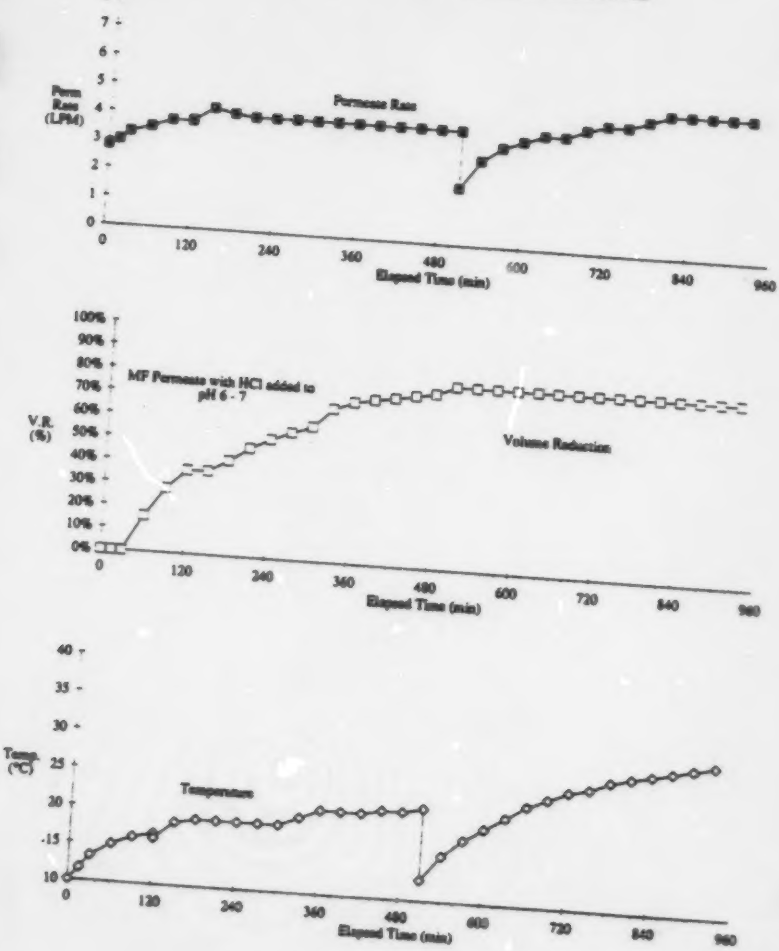

Table 1 - Process Rejections for Test #12

Component	MDL	Raw Leachate	Lime Treated Feed	MF Permeate	% MF Rejection	RO Permeate	% RO Rejection	Total Process Rejection
pH (@ 20 °c)		5.96	8.82	7.42	-	5.79	-	-
Alkalinity (mg/L)		180	950	430	54.7%	20	95.3%	97.9%
TOC (mg/L)	1	158	170	200	-	11	94.5%	93.5%
COD	10	430	470	440	6.4%	43	90.2%	90.9%
BOD5		230	-	245	0.0%	14	94.3%	-
TDS	10	530	630	600	4.8%	130	78.3%	79.4%
TSS	10	230	1200	<	>99.2%	<	-	>99.2%
Fluoride (mg/L)	0.1	<	<	<	-	<	-	-
Chloride	0.2	21	22	22	0.0%	35	-	-
Nitrate (as N)	0.2	<	<	<	-	<	-	-
Bromide	0.8	<	<	<	-	<	-	-
Phosphate (as P)	0.8	<	<	<	-	<	-	-
Sulphate	1	1.8	2.2	2.3	-	<	>56.5%	-
Calcium (mg/L)	0.023	72	230	69	70.0%	8.9	87.1%	96.1%
Magnesium	0.05	10	100	72	28.0%	5.7	92.1%	94.3%
Sodium	0.1	14	14	15	-	2.2	85.3%	84.3%
Potassium	0.5	22	22	23	-	3.7	83.9%	83.2%
Aluminum	0.03	0.078	0.17	0.05	70.6%	<	>40.0%	>82.4%
Barium	0.001	0.24	0.25	0.055	78.0%	0.008	85.5%	96.8%
Beryllium	0.001	0.001	<	<	-	<	-	
Boron	0.01	0.23	0.22	0.2	9.1%	0.07	65.0%	68.2%
Cadmium	0.002	<	<	<	-	<	-	-
Chromium	0.004	0.005	0.011	<	>63.6%	<	-	>63.6%
Cobalt	0.01	0.02	0.02	<	>50.0%	<	-	>50.0%
Copper	0.006	<	<	<	-	<	-	
Iron	0.01	130	170	3	98.2%	0.02	99.3%	>99.9%
Lead	0.02	<	<	<	-	<	-	-
Manganese	0.005	2.3	2.6	0.19	92.7%	0.03	84.2%	98.8%
Molybdenum	0.02	<	<	<	-	<	-	-
Nickel	0.01	<	<	<	-	<	-	-
Phosphorus	0.06	<	0.07	0.06	14.3%	<	>0.0%	>14.3%
Silicon	0.05	8.3	9.7	3.5	63.9%	0.35	90.0%	96.4%
Silver	0.01	<	<	<	-	<	-	-
Strontium	0.001	0.45	0.49	0.25	49.0%	0.027	89.2%	94.5%
Sulphur	0.06	1.5	3.3	2.2	33.3%	0.38	82.7%	88.5%
Thallium	0.06	<	<	<	-	<	-	-
Titanium	0.01	0.016	0.023	<	>56.5%	<	-	>56.5%
Vanadium	0.005	0.005	0.008	<	>37.5%	<	-	>37.5%
Zinc	0.005	0.009	0.038	0.018	52.6%	<	-	>86.8%
Zirconium	0.01	<	<	<	-	<	-	-
EPA624 *(µg/L)*								
trans-1,2-Dichloroethene	1.1	3.8	-	2	47.4%	1.4	30.0%	63.2%
1,1-Dichloroethane	0.5	4.8	-	2.2	54.2%	0.5	77.3%	89.6%
1,2-Dichloroethane	0.4	1.7	-	1.3	23.5%	0.9	30.8%	47.1%
Benzene	0.2	6.9	-	2.9	58.0%	0.8	72.4%	88.4%
Trichloroethane	0.3	2.4	-	1.1	54.2%	1.5	-	37.5%
Toluene	0.3	120	-	72	40.0%	14	80.6%	88.3%
Tetrachloroethene	0.2	1.1	-	0.8	27.3%	0.49	38.8%	55.5%
Ethylbenzene	0.3	22	-	11	50.0%	2.8	74.5%	87.3%
EPA-625 *(µg/L)*								
Phenol	1.1	300	-	66	78.0%	91	-	69.7%
Naphthalene	0.3	<	-	99	-	24	75.8%	-
Acenaphthene	0.7	32	-	88	-	24	72.7%	25.0%
Fluorene	0.3	24	-	46	-	6.1	86.7%	74.6%
Phenanthrene	0.3	14	-	24	-	7.8	67.5%	44.3%

MDL - minimum detection limit
< - less than MDL

C8

SLOW RATE INFILTRATION LAND TREATMENT AND RECIRCULATION OF MSW LANDFILL LEACHATE IN ONTARIO

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1. INTRODUCTION

This paper outlines the major results from a 3-year research program (1987-90) conducted by the University of Guelph for the Research and Technology Branch of the Ontario Ministry of the Environment (M.O.E. Project 333G). An interdisciplinary approach was used in this research program in applying established and proven principles and technologies from the natural sciences, particularly agronomy and silviculture ("agroforestry"), in the study of the treatment and disposal of municipal solid waste (MSW) landfill leachates on decommissioned refuse cells or adjacent land areas in Ontario (McBride, 1990).

Slow rate infiltration land treatment systems are designed to circulate wastewater back into the terrestrial (soil-vegetation) ecosystem in such a way that the maximum degree of renovation and attenuation of contaminants is achieved before the effluent re-enters the hydrologic cycle as deep drainage and phreatic water. The ecosystem thus acts as a "living filter" in effecting both physico-chemical and biological decontamination, with soil water recharge and plant nutrient supply being potential ancillary benefits.

The research program had three objectives:

i) to evaluate slow rate infiltration land treatment of leachate in forested or agricultural ecosystems using alternative land application techniques as a practicable economic, environmentally-sound and long-term solution to landfill seepage occurrences under Ontario biophysical and climatic conditions.

ii) to evaluate the recirculation of leachate to the landfill surface as a partial on-site treatment method under Ontario climatic conditions.

iii) to place the technical findings of this study within the context of land use planning for wastewater treatment and disposal.

2. RESULTS AND DISCUSSION

2.1 Characterization of Soil Microbial Responses to MSW Landfill Leachate Irrigation

A soil microbial response study was undertaken to assist in evaluating slow rate infiltration land treatment as an environmentally-sound method of treating MSW landfill leachate. Since it is generally understood that microbial organisms are central to nutrient cycling processes in the soil, emphasis was placed on both the activity and population dynamics of indigenous soil bacteria in both natural forest and agroforestry grassland ecosystems. It was presumed that if leachate had a detrimental effect on soil microbial populations, a reduction in the efficiency of energy transfer and nutrient cycling would occur. A reduction in the efficiency of the biological treatment of the wastewater over the longer term would also be likely.

The activity of the indigenous soil microbial populations was studied in situ using the alkali absorption technique. Soil respiration has been highly correlated with the general decomposer microbial population and has been shown to be relatively sensitive to different forms of toxic contamination. Soil microbial biomass was measured by the direct extraction method. This method has been used extensively to reveal alterations in microbially-active soil environments brought about by a wide variety of stresses, both natural and anthropogenic. An indication of the levels and nature of the microbial populations present within the soils was obtained using the dilution plate-count method and a morphological system of classification. This method has been widely used to elucidate the effect of various pollutants on soil bacterial populations.

This study revealed that the application of MSW landfill leachate to both forest and grassland ecosystems resulted in an increase in soil respiration. Furthermore, the magnitude of the increase in CO_2 evolution was directly related to the rate of MSW landfill leachate application. Other research has shown a high correlation between the levels of available soil organic matter and microbial activity. It is reasonable to conclude that the increase in observed soil respiration was a function of the application of an irrigant containing ample readily available substrates to the soil. The mode of irrigant application also had a significant effect on the soil respiration rates measured, with sub-surface irrigation generally yielding the highest respiration rates.

As apparent with soil respiration, the application of MSW landfill leachate to the soil resulted in an increased number of soil bacterial isolates. This is most likely due to the introduction of easily decomposed organic substrate materials in the leachate. It is also likely that the application to the soil of a supplemental microbial population present in the leachate itself may cause an increase in microbial numbers over and above indigenous soil populations. Few significant trends were evident, however, when comparing the distributions of morphological classification groups within areas which were previously sprayed with either leachate or water or in areas which served as rain-fed, environmental controls.

Conversely, soil microbial biomass tended to decrease with the application of MSW landfill leachate to both forested and grassed soil areas. These trends are similar to those reported in the summary report of M.O.E. Project 244G (McBride et al., 1988), where the effect of leachate spray application to a natural forested ecosystem at Muskoka Lakes was investigated. Other research has shown a similar chronic and inhibitory effect on soil microbial biomass with the application of sewage sludge with a high heavy metal content.

2.2 Characterization of Vegetative Responses to MSW Landfill Leachate Irrigation

A study of the physiological responses of hardwood species to irrigation by municipal solid waste (MSW) landfill leachate was conducted in a series of experiments offering a variety of measurement conditions and leachate types. In a natural forested ecosystem, an examination was made of the foliar gas exchange, water relations and spectral properties of understorey sugar maple (*Acer saccharum* Marsh.) sapling leaves subjected to spray irrigation of the Muskoka Lakes leachate. Photosynthetic rates in irrigated saplings were reduced 34% to 53%. Water use efficiency of sapling leaves subjected to direct leachate exposure dropped an average of 70% while leaf temperatures increased 20% and transpiration rates remained constant. Spectral patterns of understorey leaves with leachate residue demonstrated increased absorbance in the near infrared waveband and reduced reflection in visible wavebands. The adaxial spectral properties of mid-canopy leaves (above maximum spray height) of mature sugar maple trees had spectra that suggested increased vigour and benefit derived from leachate irrigation.

A greenhouse experiment examined the response of hydroponically grown red maple (*Acer rubrum* L.) saplings to a series of 4 sub-irrigation treatments with untreated Guelph leachate or deionized water.

Photosynthetic rates in water-treated saplings rapidly declined to 62% of the levels measured in untreated saplings, but returned to original levels in subsequent treatments. Photosynthesis in leachate-treated saplings remained at levels 50% of that of untreated saplings throughout the treatment period. Water treatment had virtually no effect on foliar element uptake or spectral response. Leachate treatment decreased the foliar content of many macro- and micro-nutrients significantly and spectral measurements indicated declining vigour. Foliar levels of some chemical constituents present in high concentrations in the leachate irrigant, such as Cl^-, rose significantly.

A third segment of the study investigated the photosynthetic and growth response of red maple and hybrid poplar (*Populus* sp. nigra X maximowiczii) to irrigation of the Glanbrook leachate under controlled field conditions, where many of the leachate constituents identified previously as being detrimental to vegetative vigour were either in lower concentrations or were naturally attenuated by the high clay content soil. Mean seasonal photosynthesis rates increased in both species irrigated with water or leachate relative to the rain-fed control saplings. Mean seasonal photosynthesis rates for red maple increased with irrigant application rate but were unaffected by irrigant type. Diameter and height growth were also largely unaffected. Mean seasonal photosynthesis rates for poplar were unaffected by irrigant application rate or type but growth increased significantly with leachate application.

2.3 Leachate Storage and Recirculation through Refuse Cells

Continuous recirculation of the Guelph and Muskoka Lakes landfill leachates through a vegetated clay surface cover was field tested in 39 bottom-draining lysimeters over two field seasons. The more concentrated of the two leachates had an osmotic potential of about -1 kJ kg^{-1} (or MPa), an electrical conductivity of 0.8 to 1.0 S m^{-1}, a chemical oxygen demand of 9.9 to 18.7 g kg^{-1} and a pH of 6.5 to 7.0. Vegetation tested included reed canarygrass (*Phalaris arundinacea* L.), meadow foxtail (*Alopecurus pratensis* L.), weeping willow (*Salix babylonica* L.) and hybrid poplar (*Populus* sp. nigra X maximowiczii). Leachate recirculation stimulated height growth by 36% to 141% in the four species tested relative to the growth observed in the water-irrigated control plants. Chlorosis of early season foliage and widespread necrosis and leaf desiccation were visible in leachate-irrigated hybrid poplar and weeping willow saplings after a total leachate application over two seasons of 740 mm. Leaf senescence in the hybrid poplar saplings preceded the normal senescence date by 5-6 weeks. By the second field season, stomatal conductance was reduced by 73%, photosynthesis rate by 63% and transpiration rate by 68% in leachate-irrigated hybrid poplar sapling leaves relative to the water-irrigated controls. Vegetative stress was most likely a result of osmoregulation disruption arising from a depressed soil solution osmotic potential. In the reed canarygrass swards, total actual evapotranspiration over the second field season was increased by 50%, height growth by 87%, and foliar biomass production by 160% through recirculation with the more concentrated Guelph leachate in comparison to the water-irrigated reed canarygrass. No phytotoxic symptoms or excessive trace metal accumulations were observed in reed canarygrass leaf tissue. Reed canarygrass shows good potential as a cover vegetation species for leachate recirculation sites under northern temperate climatic conditions.

The field saturated hydraulic conductivity of the silty clay surface covers irrigated with landfill leachate, measured to be in the order of 10^{-5} m s^{-1}, showed a significant increase relative to the water-irrigated surface covers after a cumulative total irrigant application of 2.9 pore volume equivalents. Volumetric shrinkage of the clay-rich soil cover due to increased effective stresses induced with the application of leachates containing organic solvents and salts was thought to be the cause.

As part of the above recirculation experiment, landfill leachates from these two sources were stored in 200-L holding tanks at ambient temperature for a period of several months at a time. Leachate was removed periodically to irrigate the lysimeters and the recycled irrigants were analyzed for volatile compounds. In the first year, the degradation of chlorinated solvents such as trichloroethylene and tetrachloroethane was apparent with the presence of some of their metabolites, such as cis-1,2-dichloroethene and vinyl chloride. In contrast, the levels of aromatic hydrocarbons remained constant throughout the experiment. These findings are consistent with the generally observed behaviour of these wastewater constituents under anaerobic conditions.

These results were verified during the second year of the recirculation study. In addition, the chlorofluorocarbon Freon-113 was added to several of the holding tanks to monitor its possible biodegradation. The degradation products dichlorotrifluoroethane and chlorotrifluoroethene were observed after two weeks of incubation in the holdings tanks. These compounds were first detected in Ontario in groundwater contaminated by a chemical dumpsite and, up until that time, Freon-113 had been considered refractory to biodegradation. Organic contaminants were also found to breakthrough the 50-cm deep clay layer in the lysimeters independently of their solubility and retardation factors. This indicates that preferential flow probably occurred through fissures in the clay.

These findings are of interest for the management of landfill leachates because an anaerobic incubation period as a pretreatment step would allow for the degradation of most of the chlorinated solvents. This study also demonstrates that surface clay covers, and possibly bottom liners, may not be a completely reliable means for the prevention of groundwater contamination arising from landfilling operations.

2.4 Physical and Chemical Soil-Leachate Interactions

The inorganic chemical composition and trace heavy metal speciation of four Ontario MSW landfill leachates were investigated. Chemical (and toxicological) analyses showed that the Guelph leachate was the most potent or concentrated and the Leamington leachate was the most benign of the four tested. The Cd concentration of all of the leachate samples exceeded the maximum acceptable level for potable water. The equilibrium chemical computer model GEOCHEM was used to calculate the speciation of trace heavy metals in the landfill leachates. Heavy metals existed as free metals or as complexes with carbonates, hydroxides, chlorides or sulphates. Chloride complexes dominated the aqueous chemistry of leachate cadmium. The retention of cadmium by six soils as a function of pH and initial solution Cd concentration was investigated by adsorption experiments using a batch method. The adsorption behaviour of Cd conformed to the commonly reported pH-dependent adsorption edge. The results of the adsorption experiments were modelled using two surface complexation models. The humic acid model assumes that soil organic matter behaves as a diprotic acid, and the constant capacitance model estimates adsorption on variable charge mineral surfaces. For the six soils examined, humic surfaces are the more reactive at lower pH levels and mineral surfaces become dominant at higher pH levels.

A soil slurry consolidation test protocol was developed that can be used as a pre-screening procedure to determine the degree of physico-chemical compatibility between various combinations of MSW leachates and natural soil materials potentially destined for use as landfill liners or covers. A comparative decline in total porosity was induced in a clay-rich soil material suspended in Guelph leachate, relative to a distilled water soil slurry, where both were subjected to a range of static loads up to 100 kPa. This led to a corresponding increase in soil strength as the total soil porosity declined, most likely due to the processes of osmotic consolidation and/or osmotic-induced consolidation of the phyllosilicate soil fraction. Under lower overburden pressure conditions, such as on a surface clay cover on a landfill, landfill leachates with a very negative solute potential could cause volumetric shrinkage of the soil matrix and allow preferential flow to occur through the soil.

2.5 Site Selection for the Treatment/Disposal of Leachates on Land

The Soil Potential Rating (SPR) system is a soil-based interpretive classification system that has been developed to rate the relative quality of a soil to support a particular use. Its main advantage over traditional land capability/suitability rating systems is that it emphasizes the concept of potentials or opportunities for use, rather than solely site and soil limitations or constraints.

A methodology was developed for applying the SPR system to the problem of rating soils for their ability to support the land treatment of landfill leachate. Each parameter in the SPR equation was redefined to include both economic costs and measures of environmental quality. A pilot-scale field study at the Muskoka Lakes landfill site was designed to generate soil potential indices (SPI) for three treatment options: spray, trickle and sub-surface irrigation. Each SPI was derived from sub-indices that include ratings of soil performance (P), measures that reflect the type of irrigation system, or "corrective measures" (CM), and consideration of residual effects, or "continuing limitations" (CL), on the environment. The SPR equation incorporates these sub-indices as follows: SPI = P - (CM + CL).

The careful definition of each sub-index can provide valid, detailed and locally appropriate information that planners need to improve land use decision making with respect to waste management problems. This investigation further illustrated how economic costs and less tangible values, such as the quality of "valued ecosystem components", can be combined in the local level land evaluation process. This methodology can provide valuable input to the MSW landfill site selection process in Ontario, as well as recognition of the need for planning contingencies for treatment and disposal of leachate on adjacent land.

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C7

Determination of Hydrogeological and Contamination Transport Properties of Fractured, Weathered Leda Clay in Eastern Ontario.

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Much of Eastern Ontario is underlain by the Leda Clay, a relatively soft, "impervious" clay of variable thickness. The uppermost part of the clayey deposit is weathered and fractured, up to a few meters, through which pathways exist for contaminant migration. At present, little published information is available on the degree of hydrologic activity in the fractured Leda Clay zone. Burial of municipal or industrial waste in clayey deposits is presently viewed as a safe alternative in preventing extensive migration of contaminants. However, the presence of an active hydrogeological fracture network could provide a lateral and vertical pathway for migration. Due to the recent concern of DNAPL contamination, it is even more necessary to characterize the vertical extent of the fracture network in the Leda Clay. It is therefore our objective to define the depth of fractures and quantity the fracture flow in areas having different thicknesses and depositional environments within the Leda Clay. We will also assess newly developed techniques for determining the depth of the hydraulically active fractured clay. The principal field investigations and the analysis of field data will be conducted during the summer and fall of 1990. We expect that by the beginning of 1991, sufficient data should have been acquired to define the depth of active groundwater zone and to determine whether the new monitoring techniques are appropriate for the Leda Clay.

C8

THE CHARACTERIZATION OF TWO DISCRETE HORIZONTAL FRACTURES IN SHALE

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INTRODUCTION

The quality of water supplies in Southern Ontario is threatened by contaminants, originating from landfills and industrial sites, migrating through fractures within shale bedrock. Discrete fractures which are continuous over large areas often control the fate of contaminants in the bedrock. Flow and mass transport through fractures is generally characterized using a conceptual model whereby the fracture walls are approximated by two smooth parallel plates separated by a uniform opening (aperture). Previous studies have shown that even in relatively small areas this simple conceptual model may not be appropriate and may lead to large errors in the estimation of groundwater velocity (Raven and Gale (1985); Tsang and Tsang (1987); Brown (1987); Novakowski (1988)).

Factors which may lead to deviations from the parallel plate model include fracture surface roughness, tortuosity of the flow paths and fracture contact area. The fracture contact area and the tortuosity of the flow paths is dependent on both the stress and displacement of the two fracture walls. The roughness of a fracture surface is due to the nature of the cracking process or the presence of fracture infilling materials or combination thereof. The variation of hydraulic aperture or hydraulic conductivity in fractured rock can be studied at a number of different scales ranging from the microscopic scale (eg. Brown, 1987) to a rock mass scale in the order of hundreds of metres (eg. Raven, 1986). A considerable amount of research has been undertaken in studying the nature of small-scale fracture roughness (Brown et al. (1986); Brown (1987)). Differences between hydraulic apertures and apertures calculated from surface profiles have been attributed to fracture closure (Brown, 1987). Contact area may take the form of abraded areas or single points of contact or a combination of both depending on the mode of fracture formation. Laboratory and modelling studies of natural rock surfaces (Brown and Scholz, 1985; Raven and Gale, 1985; Pyrak-Nolte et al., 1987; Tsang and Tsang, 1987) have shown that as the contact area increases, the parallel plate model provides a poorer description of fracture flux. When the contact area is greater than 30% of the total area, the flow rate can be depressed by two or more orders of magnitude than would be predicted by the cubic law (Tsang, 1984). The more small apertures there are in the distribution the larger the effect of tortuosity and thus the more error in the estimation using the cubic law (Tsang, 1984).

The description of the spatial variability of geological parameters, such as hydraulic aperture, can be accomplished using geostatistics. Many geological properties such as transmissivity, or fracture aperture fit normal, lognormal or exponential distributions on a spatial or time dependent scale. However, some researchers have found aperture distributions to be skewed. Tsang and Tsang (1987) fit a gamma function to an experimentally derived aperture distribution in a single fracture. Raven (1986) determined a skewed log-normal distribution for a fractured rock mass over a scale of the order of hundreds of metres.

An initial step in the analysis of distributions in order to estimate the parameter at points or areas where no data exists, is the construction of semivariograms (commonly called variograms). Variograms describe the variance of the increment between points in space and depend only on the distance between pairs of sample points. The construction of the variogram assumes that the parameter studied is a random function interpreted as a stationary regionalized variable. An assumption of stationarity implies that the property of the medium is stationary in space and has a constant mean (does not vary with a translation). Weak stationarity refers to a medium where only the mean and variance are stationary at any point in the medium (de Marsily, 1986). These assumptions lead to the 'intrinsic hypothesis' needed for the construction of variograms. The scale at which the data points are correlated can be inferred by fitting an experimental variogram to a theoretical model. Correlation length can be looked upon as being the spatial range within which apertures have similar values. 'Kriging' is a method of interpolating between known data points using a linear unbiased estimator. A thorough discussion of geostatistical methods including kriging is beyond the scope of this report but can be found discussed in detail by Delhomme (1978), Delhomme (1979) and de Marsily (1986).

The purpose of this study is to characterize in detail two discrete fracture zones continuous in an area of about 400 square metres. At this scale the variation of aperture in single fractures can be examined by determinations of hydraulic apertures using in-situ single well tests in different boreholes several metres to tens of metres apart. The aperture distributions determined in this study provide field data at a scale important in investigating flow and mass transport in fractured sedimentary rock. Constant-head injection tests were conducted in 25 boreholes intersecting both fracture planes in order to obtain measurements of the hydraulic aperture. Variograms are constructed for each fracture showing the level of correlation between aperture determinations in different boreholes. Previous work at this site is summarized in Novakowski (1988).

FIELD STUDY

The study site is located in the town of Clarkson, 50 km west of Toronto, Ontario and approximately 1.5 km north of Lake Ontario. The site is underlain by about 3 m of overburden which is in turn underlain by the Upper Ordovician Meaford-Dundas shale. The shale is highly weathered and fissile near the bedrock surface. Most of the fractures evident in core are bedding plane partings associated with soft mud seams or interbeds of siltstone and fossiliferous dolostone of up to 0.20 m in thickness. The fractures are flat-lying and probably formed as sheeting structure along the bedding planes. During the last four years, a total of 25 boreholes, each 0.038 m in diameter, arranged in a 20 m x 20 m grid (five lines with five boreholes in each line) have been completed at the site (Figure 1). Previous work at the site (Blackport et al., 1986; Mase et al., 1987 and Novakowski, 1988) has led to the identification of two fracture zones which are the focus of current studies. The two fractures or fracture zones are referred to in this report as the upper and lower fracture respectively.

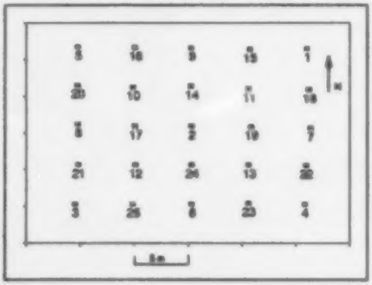

Figure 1: Site map showing all boreholes (boreholes are numbered in the order of completion).

The upper fracture is located approximately 9.8 m below ground surface while the lower fracture is approximately 10.5 m below ground surface. The lower fracture is associated with a fossiliferous dolostone bed which varies in thickness between 0.10 m and 0.18 m across the site. The upper fracture is also associated with a dolostone bed which was identified in 11 boreholes and is less than 0.05 m in thickness.

In order to obtain hydraulic aperture measurements for each of the two fractures in each of the 25 boreholes, constant-head injection tests using packer spacings of variable length were carried out. A constant-head injection test is conducted by injecting water into a portion of the borehole sealed off between two inflatable packers and measuring the resulting change in pressure at a constant flowrate. Since the vertical distance between the two fractures is approximately 0.70 m, packer spacings less than this distance were employed to ensure that the two fractures were measured separately. A more detailed explanation of the general field methodology employed for constant-head injection tests can be found in Zeigler (1976); Doe _et al._ (1980) and Doe and Remer (1987). A description of the specific testing methodology employed for this study can be found in Novakowski (1988).

METHODS OF ANALYSIS

Fracture aperture can be determined from constant-head injection tests by using a modified version of the Theim equation for steady state radial flow and the cubic law (Witherspoon _et al._, 1980). Fracture aperture is calculated using the following:

$$2b=\left(\frac{Q}{\Delta H}\cdot\frac{6\mu}{\pi\rho g}\right)^{\frac{1}{3}}\cdot 1x10^{-6} \qquad (1)$$

where 2b is aperture (μm), Q is the steady state flowrate (m^3/s), ΔH is the difference in hydraulic head between static initial conditions and a steady flow condition (m), r_e is the radius of influence (m), r_w is the radius of the well (m), ρ is the fluid density (kg/m^3), g is gravational acceleration (m/s^2) and μ is the kinematic viscosity (m^2/s). It is assumed that the results of the constant-head tests represent an average value of the aperture immediately adjacent to the borehole (Novakowski, 1988).

To analyze the statistical nature of the aperture distribution in each of the two fractures, variograms were constructed using the results of the constant-head tests. The experimental variogram can be estimated for values of h which are multiples of a unit distance (lag) by using (Delhomme, 1978):

$$v(h)=\frac{1}{2N(h)}\sum_{i=1}^{N(h)}\left(z(x_i+h)-z(x_i)\right)^2 \qquad (2)$$

where v(h) is the variogram, $z(x_i)$ are the experimental values at points x_i such that data are available both at x_i and x_i+h and N(h) is the number of pairs of data points separated by a distance h. Since there was insufficient data suggesting otherwise, the data was assumed to be isotropic. Thus, it was assumed that there was no directional variation in the aperture distributions and that the variations were a function of distance only. This assumption allows the lag distance to be treated as a scalar and the distribution as one dimensional. Pairs were examined using lag distances which are multiples of the shortest distance between two boreholes. The natural logarithm of aperture (Ln(2b)) was used. A total of 160 pairs for each fracture are possible by using the four directions, N-S, E-W, N45E and N45W across the borehole grid. Four lag distances are possible in the N-S and E-W directions and another four in the N45E and N45W directions to obtain a total of 8 lag points from the 160 pairs. Lag distances range from 5.3 m to 30 m.

Three theoretical models are commonly used to fit to experimental variograms. These include a spherical model, an exponential model and a linear model (Delhomme, 1978). By fitting the experimental variogram to a theoretical model, correlation parameters can be determined which can be used for further interpretation and modelling such as kriging.

RESULTS AND DISCUSSION

Over 250 constant-head injection tests were completed this spring in order to determine the location and aperture of both fractures in all of the boreholes. A summary of fracture aperture widths is shown in Table 1. The distribution of apertures in the lower fracture ranges from 282 micrometers to below detection limit. In the upper fracture apertures range from 138 micrometers to below detection limit. The detection limit for this particular testing system is estimated to be approximately 10 micrometers. The large number of non-detectable apertures results in multi-modal

Table 1. Summary of fracture aperture widths (in micrometers) as determined from the results of constant-head injection tests.

Borehole #	Upper Fracture 2b(μm)	Lower Fracture 2b(μm)	Borehole #	Upper Fracture 2b(μm)	Lower Fracture 2b(μm)
1	90	221	14	106	241
2	66	235	15	94	26
3	138	27	16	<10	<10
4	67	220	17	104	<10
5	<10[a]	226	18	18	<10
6	80	85	19	<10	248
7	115	98	20	39	243
8	62	15	21	<10	18
9	<10	167	22	58	282
10	<10	<10	23	120	57
11	107	126	24	54	154
12	<10	94	25	120	214
13	<10	<10			

[a] aperture is below measurement limit of testing system

distributions (Figures 2 and 3) and thus the apertures are not normally or log-normally distributed as is commonly postulated at this scale (eg. Gale et al.,1985).

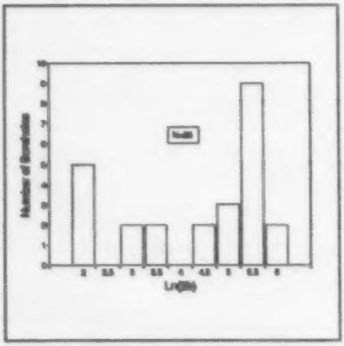

Figure 2: Distribution of apertures for lower fracture.

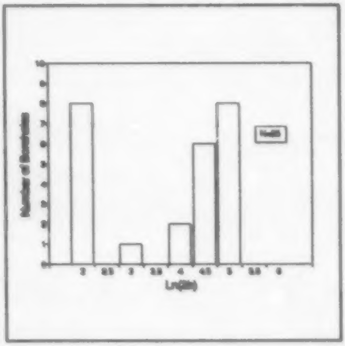

Figure 3: Distribution of apertures for upper fracture.

In 25% of the boreholes the aperture of the lower fracture was below the detection limit and in 32% of the boreholes the aperture of the upper fracture was below the detection limit. This result is interesting and suggests that a scale effect may influence the measurement of the aperture distribution. The reason for the large number of small to non-existent apertures is probably a result of the nature of the proppage of the fracture. For example, this particular area of Southern Ontario, is neo-tectonically active with high compressive-stress oriented horizontally (Lo, 1978). Dynamical stress changes can cause repeated shearing of a small scale in the plane of the fracture. Thus, over time, the asperities or points of contact along the fracture become abraded and flattened. Consequently, the area of contact is increased resulting in a bias towards smaller apertures.

The variograms for both fractures are shown in Figures 4 and 5. For the purpose of variogram construction apertures below detection limit were given a value equal to the detection limit (10 µm). In constructing the variograms for the upper and lower fractures all data pairs were used. This means that a different number of pairs were summed for each lag distance on the variogram. For example, at a lag distance of 5.3 m (distance between two adjacent boreholes in a N-S or E-W direction) 40 pairs are possible. However, at a distance of 21.2 m (4 x lag distance) only 10 pairs are possible. No attempt was made to adjust the number of pairs used at each given distance and therefore some bias may be introduced in the analysis.In addition, and perhaps of more severe consequence, the multimodal distribution of apertures may influence the nature of the variogram. Because there is no identified similar examples in the literature, it is assumed that for the following discussion, the variograms are constructed using a log-normally distributed aperture.

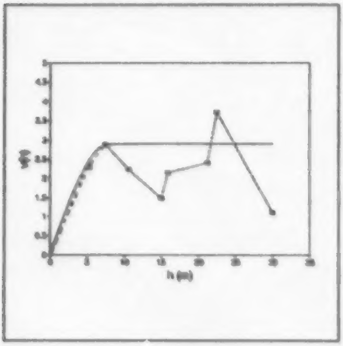

Figure 4: Variogram using aperture distribution of lower fracture.

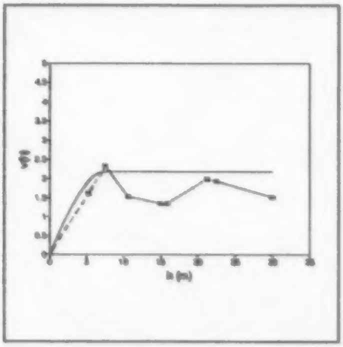

Figure 5: Variogram using aperture distribution of upper fracture.

A spherical model was chosen to fit against the experimental variograms for both fractures. The equation for the spherical model fit is as follows (Delhomme, 1978):

$$\begin{aligned}\gamma(h) &= \omega\left(\frac{3}{2}\frac{|h|}{a}-\frac{1}{2}\left(\frac{|h|}{a}\right)^3\right) & h\leq a \\ &= \omega & h>a\end{aligned} \tag{3}$$

This model was chosen assuming that the experimental variograms went through the origin and attained a sill around 10 m. The distance at which the variogram attains the asymptote (or sill) is referred to as the range and shows the extent of the zone of influence of an experimental point (Delhomme, 1978). Using the model fits in Figures 4 and 5 a range of 8 m was determined for the lower fracture and a range of 7.5 m for the upper fracture respectively. This suggests that only the boreholes immediately surrounding a given borehole are spatially correlated. Furthermore, because of the approximate nature of the model fits, correlation lengths much smaller are equally possible. Further work is necessary in order to investigate both the sensitivity of various model fits and the appropriateness of the chosen model, in addition to the aforementioned problem of the nature of the distribution.

Because determination of a correlation length from the aperture statistics is inconclusive, fracture closure was examined in terms of radius of influence of the hydraulic tests. It was assumed that the radius of influence of a particular hydraulic test could range radially from 0.038 m (one wellbore radius) to a maximum of 2.65 m (half of the distance to the nearest neighbouring borehole). A total fracture area was calculated as 25 m x 25 m square (the area of the grid extended the half distance between boreholes in all directions). The percentage of each fracture plane which is closed can then be calculated assuming that each non-detectable aperture has an equal effect on the total fracture plane. Total fracture contact area is calculated based on a sum of all non-detectable aperture areas.

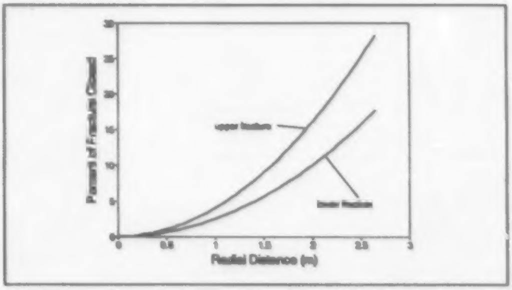

Figure 6: Diagram showing the percent contact area with varying radius of influence of the hydraulic tests.

The purpose of this calculation is to examine the difference in possible contact area based on the radius of influence of the hydraulic tests. In the upper fracture plane a maximum of 28% of the fracture plane may be closed while in the lower fracture a maximum of 18% of the fracture plane may be closed (Figure 6). As both fractures occur at shallow depths (less than 15 m) it seems unlikely that lithostatic pressure (<1 MPa) alone would lead to such large areas of fracture closure. Large areas of closure suggest tortuous flow paths may affect the average velocity of groundwater and contaminants through the fractures and lead to a highly dispersive system. The two curves show that there may be significant differences between the two fracture zones.

SUMMARY

The uncertainty and ambiguous nature of the descriptions of the aperture distributions and variograms in this study indicate that the processes and conditions which lead to fracture formation need to be examined and taken into account in any model of the fracture flow field. The large number of non-detectable apertures found in both fractures suggests potentially large areas of closure. The nature of these areas of closure will have significant effect on mass transport and velocity determinations in single fractures. Previous tracer tests at the site (Novakowski, 1988) found large measurements of dispersion which may possibly be attributed to tortuous flow paths around areas of closure. Kriging the fracture zone planes will yield various simulations of the aperture distributions of the fractures over the study site. Further work is needed to examine the aperture distributions in a stochastic framework in order that realistic models for groundwater velocity and contaminant transport within both of the fracture zones studied can be determined.

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The Origin and Distribution of Methane in the Alliston Aquifer Complex.

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INTRODUCTION

The main components of the carbon cycle in groundwater are dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) and a common trace component seems to be methane. However, this hydrocarbon could become a major carbon pool and a potential (explosive) contaminant where is present in high concentration (Coleman, 1976; Barker, 1979). This seems to be the case for groundwater in some parts of the Alliston Aquifer Complex. Many wells that tapped this aquifer produce high volumes of methane. As a result, most of the municipal wells have aeration treatment systems. However, the origin and distribution of methane in this aquifer is not well established.

The presence of methane in groundwater could be associated to in-situ production by reactions mediated by bacteria (methanogenesis) and/or migration of gases from bedrock reservoirs. The last type is called thermocatalitic and is formed by decomposition of organic matter at relative high temperature. Both types of methane are categorized as biotic gases (participation of organic matter in methane formation).

Two hypotheses have been postulated to explain the occurrences of methane in the Alliston Aquifer. One suggests that the occurrence of methane is controlled by the nature of the underlying Paleozoic bedrock. Where the bedrock is shaley (Collingwod, Blue Mountains Groups), insignificant amounts of gas are found. However, where the bedrock is limestone (Trenton Group), methane is found at high concentration. This implies that the source of methane is leakage or migration from the more permeable limestone bedrock. This hypothesis is supported by the fact that methane is likely present in the Trenton Group. It is well documented that these carbonate rocks are an important reservoir for natural gases in other part of Southern Ontario (Barker and Pollock, 1984).

The second hypothesis, based on carbon isotope analyses of methane from some overburden wells, suggests that methane is biogenic, produced by bacterial action. This implies that the methane is produced within the aquifer, since the methane found in the Trenton rocks has an isotopic composition typical of thermocatalitic methane. Therefore, a bedrock control of the occurrence of methane appears to be unlikely.

This paper presents a summary of results from a research project funded by the Ministry of the Environment, whose main objectives are, to establish the distribution pattern of methane, to determine the origin of methane and to establish a basis for prediction of methane occurrences in the aquifer.

STUDY SITE

This research has been carried out in the Alliston Aquifer complex. This aquifer is a confined, discontinuous, but extensive network of fine to gravelly sand lenses underlain by bedrock or basal till and overlain by clayey till. It seems the aquifer extends from the vicinity of Aurora to Wasaga beach and includes the area nortwest along the Nottawasaga Bay (Figure 1). This aquifer is the major water supply for towns such as Alliston, Cookstown, Newmarket and Bond Head and is an essential water resource for an increasing population.

The study area is mostly underlain by rocks of the Simcoe (middle Ordovician) and Nottawasaga (upper Ordovician) Groups. The areal distribution of the various units that formed these groups is shown in Figure 2. The units relevant to this study are the Trenton and Black River Limestone and the Collingwood and Blue Mountain Shales.

APPROACH AND ACTIVITIES

The research approach includes the use of hydrological, geological and geochemical tools. The rationale for this research approach can be found in Aravena et al, 1988.

The main activities carried out during this research can be summarized as follow: A map of the bedrock lithology was constructed to test the hypothesis that the nature of the bedrock controls the distribution of methane in the aquifer; A map of the groundwater flow regime was updated to evaluate the role of the groundwater as a transport medium for the methane; Groundwater from bedrock and overburden wells was sampled to evaluate the distribution of methane; Analyses of carbon isotopes (^{13}C, ^{14}C) in methane and DOC samples were performed to provide information about the origin and carbon sources for methane; Stable isotopes (^{18}O, ^{2}H) analyses in groundwater were performed to evaluate the origin of groundwater in the aquifer.

SUMMARY OF RESULTS

Gas analyses

Chromatographic analyses of gas samples indicate that the main components of these gases extracted from groundwater are methane and nitrogen. The average concentration of these two gases are 80 % and 15 % respectively. However, in some groundwater N_2 gas is the main component. ^{15}N analyses are being carried out in some gas samples to provide information about the origin of the nitrogen. Table 1 presents gas composition data for representative gas samples from overburden and bedrock.

Methane concentration data are plotted in Figure 3 for overburden groundwater and Figure 4 for bedrock groundwater. The non continuous line represents the boundary between the limestone and the shale bedrocks. It appears that the area southeast of Alliston towards Beeton has the high concentration of methane, either in bedrock or overburden wells. A trend toward decreasing methane concentration is observed in the area north and northeast of Alliston. No methane was found in overburden and bedrock wells sampled along the west side of the aquifer.

A comparison of the regional distribution of methane with the areal distribution of the underlying Ordovician bedrock indicates that the nature of the bedrock does not influence the distribution of methane in the aquifer.

Environmental Isotopes analyses

Carbon isotope analyses in methane samples present a $\delta^{13}C$ range between -69 o/oo to -84 o/oo with most of the samples around -75 o/oo. No significant isotopic differences have been noted in methane from overburden and bedrock wells. These data are similar to that reported from some overburden wells by Barker and Fritz (1981). Figure 5 shows the $\delta^{13}C$ and $\delta^{2}H$ distribution of methane gases of different origin. All methane results from the Alliston groundwaters plot in the field of biogenic methane. Furthermore, $\delta^{2}H$ data in methane and associated groundwater indicate that the main reaction pathway for methane formation is CO_2 reduction.

Carbon sources for methane

Since DOC could be a potential carbon source for methane, an extensive evaluation of this carbon pool was carried out in the aquifer. These data show a range of DOC concentration between 1 ppm to values as high as 17 ppm (Table 1). Typical DOC concentration are less than 1 ppm in deep groundwater and less tham 5 ppm in unconfined aquifers in the Alliston area (Wassenaar, 1990). These high DOC concentration suggests that the groundwater is moving through aquifer materials that are rich in organic matter. DOC and methane concentration present a direct linear correlation, which suggest that both carbon pools are related to a common carbon source.

^{14}C analyses on DOC (hydrophobic fraction) and methane samples supports this hypothesis (Table 2). Radiocarbon ages for carbon pools are in the same age range. However, in some parts of the aquifer, DOC ages are much younger than methane ages. This suggest that methane is transported by the groundwater from production zones to other part of the aquifer. Radiocarbon ages for methane also eliminated the possibility of a significant Paleozoic bedrock carbon source for the methane.

Reports of the presence of organic matter in water well log records published by the M.O.E. also supports the idea of a carbon source for methanogenesis within the aquifer materials.

Origin of groundwater

The stable isotope data (^{18}O, ^{2}H) in overburden and bedrock groundwater is plotted in Figure 6. This plot shows an isotopic range between -14.3 o/oo and -10.7 o/oo for ^{18}O and -92 o/oo and -78 o/oo for ^{2}H. This significant isotopic difference implies that at least two types of groundwater are present in the aquifer. The isotopic composition of modern water in the unconfined shallow aquifer in the Alliston area ranges between -10.8 o/oo and -11.5 o/oo for ^{18}O and -78 o/oo and -81 o/oo for ^{2}H (Wassenaar, 1990). The presence of isotopically depleted groundwater (^{18}O = -14.3 o/oo) in the aquifer suggest that these waters were recharged during cooler climatic conditions than today.

CONCLUSIONS

The main conclusions of this research can be summarized as follow:

- The nature of the bedrock does not control the distribution of methane in the aquifer.
- Methane is formed by microbial processes (methanogenesis) and is not thermocatalitic, as is the case for many bedrock methane sources in Southern Ontario.
- Organic rich sediments present in some parts of the aquifer are the main carbon sources for methane and dissolved organic carbon.
- The distribution of methane appears to be controlled by migratory transport in groundwater from production zones to diferents parts of the aquifer.
- Old groundwater recharged under different climatic conditions than today is present in some parts of the aquifer.

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Table 1. Chemical composition of representative gas and DOC in water samples, Alliston Aquifer Complex.

WELL	ELEVATION	CH$_4$	N$_2$	O$_2$	CO$_2$	CH$_4$	DOC
	(fasl)		(%)			(uM/l)	(ppm)
BR*	569	87.8	8.25	0.14	0.91	4680	9.3
BR	430	83.2	13.8	0.3	1.15	2180	8.2
BR	470	64.5	35.5	0.80	0.44	2550	5.2
BR	405	7.2	89.3	0.04	0.22	240	0.9
BR	382	31.7	58.7	0.41	0.1	1160	2.0
OV**	574	71.9	27.4	0.50	0.85	2080	7.4
OV	503	79.8	17.8	0.45	1.13	3550	17
OV	494	82.1	13.6	1.2	2.7	2765	8.7
OV	517	44.3	45.8	0.30	0.15	1391	6.8

Table 2. Radiocarbon data of CH$_4$ and DOC from overburden and bedrock wells

WELL	ELEVATION (fasl)	MATERIAL	CH$_4$ (uM/l)	DOC (ppm)	^{14}C AGE (yrs. BP)
OV	466	CH$_4$	2750		32,700
		DOC		15	35,500
OV	503	CH$_4$	3550		29,600
		DOC		17	26,200
OV	553	CH$_4$	2650		40,000
		DOC		9	30,000
OV	511	CH$_4$	2780		28,000
		DOC		14	16,800
BR	458	CH$_4$	2550		26,000
		DOC		5	9,000

* BEDROCK
** OVERBURDEN

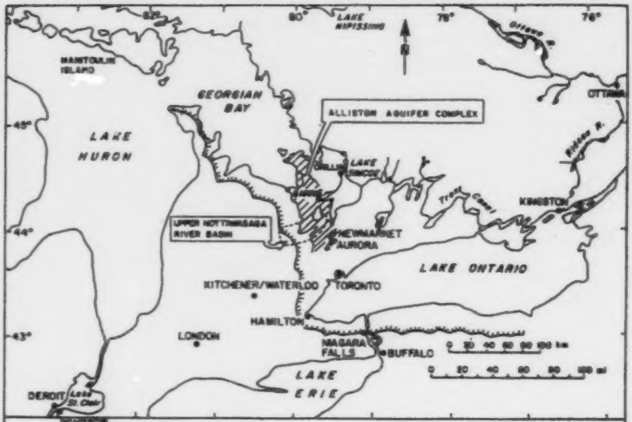
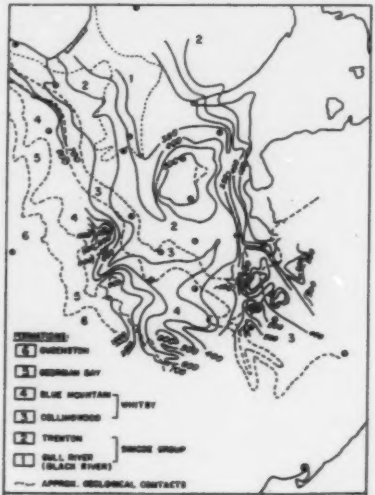

82°
80°
LAKE NIPISSING
78°
76°
N
Ottawa R.
MANITOULIN ISLAND
OTTAWA
GEORGIAN BAY
ALLISTON AQUIFER COMPLEX
45°
LAKE HURON
Rideau R.
LAKE SIMCOE
Trent Canal
KINGSTON
UPPER NOTTAWASAGA RIVER BASIN
44°
NEWMARKET
AURORA
LAKE ONTARIO
KITCHENER/WATERLOO
TORONTO
HAMILTON
43°
LONDON
NIAGARA FALLS
BUFFALO
0 20 40 60 80 100 km
0 20 40 60 80 100 mi
LAKE ERIE
DEROIT
Lake St. Clair
WINDSOR

Figure 1. Location map of the study area


2
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FORMATIONS:
6 QUEENSTON
5 GEORGIAN BAY
4 BLUE MOUNTAIN
3 COLLINGWOOD
WHITBY
2 TRENTON
1 BULL RIVER (BLACK RIVER)
SIMCOE GROUP
APPROX. GEOLOGICAL CONTACTS

Figure 2. Plan of bedrock topography and lithology.

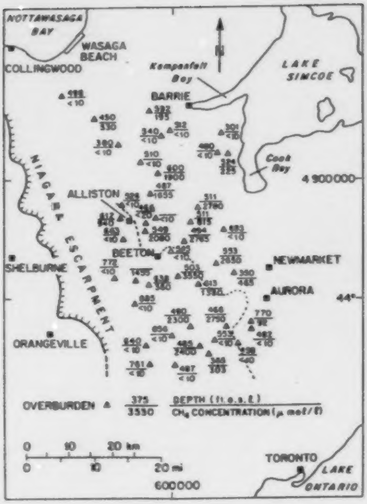
NOTTAWASAGA BAY
WASAGA BEACH
COLLINGWOOD
Kempenfelt Bay
LAKE SIMCOE
BARRIE
Cook Bay
4 900000
NIAGARA ESCARPMENT
ALLISTON
BEETON
SHELBURNE
NEWMARKET
AURORA
44°
ORANGEVILLE
OVERBURDEN
375
3550
DEPTH (ft.b.s.l.)
CH4 CONCENTRATION (μ mol/l)
0 10 20 km
0 10 20 mi
TORONTO
LAKE ONTARIO
600000

Figure 3. Sampling location and methane concentration in overburden wells, Alliston aquifer complex.

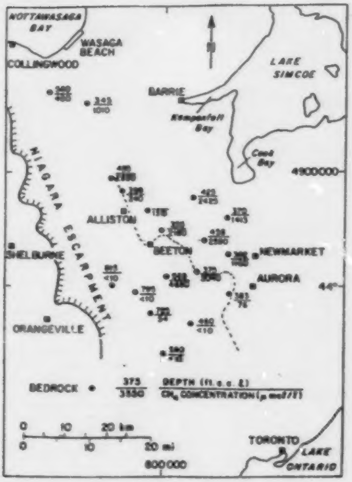
NOTTAWASAGA BAY
WASAGA BEACH
COLLINGWOOD
LAKE SIMCOE
BARRIE
Kempenfelt Bay
Cook Bay
4900000
NIAGARA ESCARPMENT
ALLISTON
BEETON
SHELBURNE
NEWMARKET
AURORA
44°
ORANGEVILLE
BEDROCK
375
3550
DEPTH (ft.b.s.l.)
CH4 CONCENTRATION (μ mol/l)
0 10 20 km
0 10 20 mi
TORONTO
LAKE ONTARIO
600000

Figure 4. Sampling location and methane concentration in bedrock wells, Alliston aquifer complex.

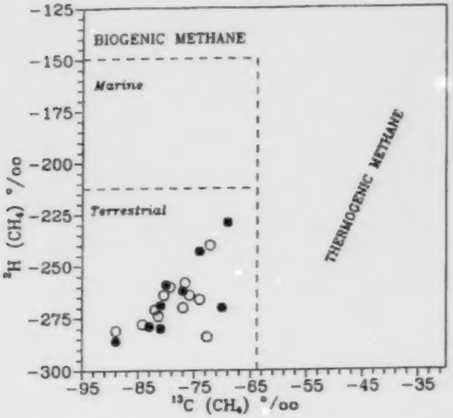

Figure 5. Relationship between the isotopic composition and genesis of methane

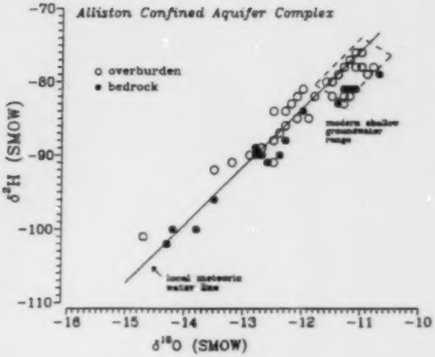

Figure 6. Oxygen-18 anddeuterium composition of groundwater, Alliston Aquifer Complex

THE RECYCLING OF STEELMAKING DUSTS USING THE LB FURNACE

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ABSTRACT

Three types of electric arc furnace dusts (with zinc oxide contents at 10, 22 and 37% wt.) and one basic oxygen furnace dust (with zinc oxide content 2.1% wt.) were treated in a bench scale LB furnace[1]. Steelmaking dusts were mixed with pulverized coal (various amounts of crushed mill scale were also added to raise the bulk density of the mixture) reduced in the reducing chamber to produce lumpy sponge which dropped by gravity to the melting chamber. In general, 20% wt of coal in the mixture is adequate to complete substantially the reduction. All CO, H_2 and zinc and lead vapours were burned in the combustion chamber to provide the heat requirements to produce sponge at 1000 C. The melting chamber is heated by plasma. Slags and liquid metal made from LB Furnace reduction contain very low amounts of zinc and lead, often at detecting limits of analytical instruments. Zinc and lead oxides in LB Furnace dusts increases with the increase of their contents in the feed materials.

1. INTRODUCTION

Every year, about four million tonnes of lead and five million tonnes of zinc are produced and consumed in the world. In our effort to recycle industrial products (using scrap in steelmaking and in nonferrous foundries) and in the disposal of municipal waste (incineration), heavy metals such as lead, zinc, cadmium, etc., resurface, usually in hazardous dusts. The most feasible solution for the detoxication of these hazardous materials lies in the volatility of of heavy metals under a reducing condition in the presence of carbon and/or hydrogen. Zinc, lead, cadmium, etc (originally in either metallic or oxidized state) will become vapours and separate from the materials being treated

The literature on disposal, recycling and recovery of steelmaking waste oxides are mainly on electric arc furnace (EAF) dusts. A collection of papers in this area[2] and a critical review of the problems and potential solutions[3] are available. Among various technology proposed two types of approaches may be identified:

(a) From high zinc EAF dust to metallic zinc

They are usually plasma (or other electrically heated) furnaces with single chamber for reaction. Combustion is avoided to minimize the amount of oxidizing gases such as CO_2 and H_2O which may cause re-oxidation in the condensation metallic vapours.

(b) From low zinc EAF dust to high zinc dust

Rotary kiln and slag fuming are common approaches. Coal is usually the energy source. It has been often suggested as the choice for regional treatment center to have the economy of size.

In the literature, two concerns have been often expressed. They are energy efficiency and the need of agglomeration of dusts.

2. THE LB FURNACE

The work on LB furnace initiated in the early 1980's at McMaster University is aimed to developed a coal-based ironmaking process using fine ore and pulverized coal(1). In order to have high energy efficiency, coal is first used as reductant then as a fuel. The advantages include large reacting surfaces, no agglomeration nor coking is required and very high energy efficiency.

The LB furnace may be divided into two chambers: (1) the reduction/combustion chamber and (2) the melting chamber, as shown in Fig. 1. The former consists of the reaction tube and the combustion chamber, and the latter a plasma-heated crucible. It may be used to make sponge iron (with plasma off) and to have it melted in other types of vessels.

Mixtures of coal, dust, ground mill scale and fluxes are moved mechanically with the use of a steel screw feeder through a silicon carbide tube to the combustion chamber. The tube is 1200 mm long and 83 mm I.D. Hot gaseous products and sponge iron are discharged at the hot end of the tube in the middle of the combustion chamber. Sponge iron which is protected from re-oxidation by the outgoing hot gas until it drops into the melting chamber. The hot gas consists mainly of CO, H_2, metal vapours and very small amounts of CO_2 and H_2O. When the gas is burned in the combustion to provide heat for reduction, metal vapours are burned to oxides and collected in the baghouse.

3. EXPERIMENTAL PROCEDURES

At the beginning of each experiment, a natural gas burner is used to heat up the structure of reduction/combustion chamber for about 90 to 120 minutes. For the treatment of dust, the feeding of solids starts when the thermocouple near the hot end of the reaction tube reaches 1050 to 1100°C, the steady state temperature is 1200 to 1250°C. The cutting of nature gas to the burner begins at the time charging of solids starts and completely off in about 15 to 30 minutes. The power to plasma furnace starts at about the same time to keep the melting chamber at a temperature of 1550°C. The charge rate is about 10 kg per hour and the linear velocity of solids in reaction tube is 60 mm/min. The residence time of solids inside the combustion chamber is about 4 minutes.

4. MATERIALS

Four types of steelmaking dusts and the slag from secondary lead smelting were used for this investigation. Five concentration levels of zinc oxide in these five kinds of waste oxides, from 0.3 to over 30% wt., have been studied. Mill scale was used for two purposes: (A) there are oily mill scales to be disposed of, and (B) the addition of mill scale improves the density and strength of sponge iron. Compositions of these materials and sand are listed in Table 1. Both coal and mill scale are ground to 95% -300 μm or finer. No attempt was made to dry these materials because they appear to be very dry.

5. EXPERIMENTAL RESULTS

Experimental data of the first series of runs on low zinc EAF dust are listed in Table 2. In Table 2A, the makeup of mixtures of waste oxides, high volatile coal and fluxes are listed. In these mixtures, ranges of zinc oxide and lead oxide contents are 3.8 to 7.5 and 0.8 to 1.6% wt., respectively. The weights of reaction products (dust, slag and liquid metal) are given in Table 2B. Total dust is listed which means the sum of baghouse dust and cyclone dust, the latter contributes less than 5% in weight and slightly lower in zinc and lead contents. Reports on the weights of reaction products in all other experiments will be omitted to avoid repetition. In Table 2C, the compositions of reaction products are presented. The recovery of volatile heavy metals in the dust collected are given in Table 2D.

Results of treating EAF dusts with medium and high zinc contents are listed in Table 3. Zinc oxide and lead oxide in mixture of Exps. 11 and 17 with EAF dust of medium zinc oxide and lead oxide contents are in the range of 8.4 to 16.3 and 1.16 to 2.25% wt., respectively. The corresponding values for Exps. 21 and 22 for high zinc EAF dust are 14.1 and 3.55% wt., respectively.

Five experiments with two levels of BOF dust in the mixture were carried out, see Table 4. In Table 5, results of experiments for treating slag from secondary lead smelting are listed.

6. DISCUSSIONS

The purposes of the treatment of waste oxides with volatile heavy metals in LB Furnace are:

(1) To enrich zinc and lead oxides in LB Furnace dust so that it could be the feed for economical extraction of zinc, lead and possibly Cd.

(2) To produce iron alloys and slag to be used in steel plant or to be safely disposed.

The compositions of slag and iron alloys produced in our laboratory are listed in Table 2C, and Tables 3 to 5. They are clearly suitable for re-use or disposal.

Correlation between zinc and lead oxide in the mixture to be fed to LB Furnace and that in the dust collected are shown in Figs. 2 and 3, and the enrichment ratios in Figs. 4 and 5. One may conclude from Fig. 2 that LB Furnace will produce dust of zinc oxide at 30% or higher from all four kinds steelmaking dusts studied under a variety of conditions. From Figs. 4 and 5, the effectiveness of LB Furnace in treating low zinc and lead waste oxides are clearly shown. Lines in Figs. 2 to 5 are arbitrarily drawn. It should be pointed out that data points outside of these bands are usually that involving lead slag.

There are at least two mechanisms by which individual particles ended up in the dust collectors in LB Furnace.

(i) The re-oxidation of gaseous metals
It is almost certain that most zinc vapours, if not all, generated in the reduction tube and the rest in the melting chamber. In the combustion chamber, zinc vapour is burned along with carbon monoxide in the flame. The behaviour of lead would be essentially the same, except that in proportion, there may be slightly more lead gasified in the melting chamber because it has relatively lower equilibrium vapour pressure.

(ii) The carry-over of solid particles
Lime, iron oxide and other refractory oxides found in baghouse arrived there in fine particles and did not go through the reaction paths of gasification and reoxidation. These fine particles could be available for gas flow to carry it over to baghouse under the following two conditions:

- Lower degree of reduction which leads to a lower degree of agglomeration of sponge iron at the moment of its discharge to melting chamber, would generate dust from the fine materials in the reaction mixtures.
- The other possible mechanism is due to carbon boil in slag/metal system. It is unlikely to be important because of a relatively low level of de-carburization rate in this system.

7. CONCLUSIONS

The reduction of steelmaking dusts containing zinc oxide from 2 to 30% wt. by coal has been carried out in LB Furnace which consists of a reduction/combustion chamber and an electrically heated chamber for the melting of slag and metal. The following conclusions may be reached:

(a) Slags and metal ingots made from LB Furnace reduction contain very low amounts of zinc and lead, often at detecting limits of analytical instruments.

(b) Zinc and lead oxides in LB Furnace dust increases with the increase of their contents in the feed materials. It has been observed to be in the range from 30 to 60% wt. ZnO and from 8 to 10% wt. PbO for steelmaking dusts.

(c) The enrichment of ZnO and PbO increases with the decrease of their contents in the feed materials ranging from 45 to 5 times for ZnO and 20 to 4 times for PbO for steelmaking dusts.

(d) For the reduction of lead slag, the LB Furnace dusts could have PbO concentration as high as 50% wt., and an enrichment ratio of about 8.

8. ACKNOWLEDGEMENT

Financial supports from Ontario Ministry of Environment and Canadian Steel Environment Association are very much appreciated.

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(2) "Disposal, Recycling and Recovery of Electric Arc Furnace Dust", A collection of papers published by AIME, Iron and Steel Society, AIME (1985).

(3) "Disposal, Recycling and Recovery of EAF Dust", A report published by Centre of Metals Production, Mellon Institute, 4400 Fifth Avenue, Pittsburgh, PA, U.S.A. (1987).

Table 1: Chemical Analysis of EAF and BOF Dusts, Mill Scale, Lead Slag and Sand, in Wt.%

Oxides*	EAF 1	EAF 2	EAF 3	BOF	LEAD SLAG	MILL SCALE	SAND
ZnO	10.30	22.68	37.20	2.10	0.32	–	–
PbO	2.16	3.12	9.35	1.10	4.33	–	–
CdO	0.05	0.10	0.08	0.01	0.0002	–	–
SiO_2	3.50	3.04	2.27	2.10	11.55	0.34	55.3
Al_2O_3	0.64	1.27	0.56	0.10	3.50	0.11	1.90
FeO	45.80	36.77	25.80	63.30	61.20	73.03	1.59
MgO	5.14	2.44	1.93	5.55	1.65	0.003	3.70
CaO	20.98	15.55	14.04	23.60	6.90	0.10	18.00
Na2O	2.50	1.15	2.66	0.20	3.15	0.01	0.70
K2O	2.31	0.70	0.99	0.15	0.20	0.001	1.14
TiO_2	0.08	0.07	0.05	0.05	0.28	0.005	0.20
MnO	2.33	4.01	3.06	1.49	0.60	0.89	0.03
P_2O_5	0.19	0.11	0.14	0.06	0.68	–	–

* Chemical analysis was carried out by X-ray Fluoroescence Method.

Table 2-A: Compositions of Reacting Mixtures, % Wt.

RUN #	1	2	3	4	5	6	7	8	9
EAF 1 DUST	37.0	37.0	37.4	37.4	20.0	20.0	53.0	53.0	73.0
MILL SCALE	37.0	37.0	37.4	37.4	57.0	57.0	20.0	20.0	-
COAL	18.6	18.6	18.7	18.7	20.0	20.0	20.0	20.0	20.0
GLASS SCRAP	7.4	7.4	3.7	3.7	3.0	-	-	-	-
SAND	-	-	2.8	2.8	3.0	3.0	7.0	7.0	7.0

Table 2-B: Weights of Reaction Products, Kgs

RUN # PRODUCT	1	2	3	4	5	6	7	8	9
SLAG	2.66	2.45	3.38	2.80	1.50	1.90	2.16	2.25	2.10
METAL	7.90	6.90	6.80	7.10	6.20	7.95	3.85	4.30	3.10
TOTAL DUST	1.60	1.40	1.80	1.60	0.87	1.10	1.90	1.80	2.10

Table 2-C: Chemical Compositions of Reaction Products, % Wt.

RUN # PRODUCT	1	2	3	4	5	6	7	8	9
BAGHOUSE DUST									
ZnO	37.3	36.4	35.2	39.6	30.0	31.0	37.8	38.9	44.8
PbO	6.2	7.8	7.4	4.9	5.9	6.6	8.1	6.9	11.8
FeO	29.3	23.1	22.9	23.1	36.6	30.7	26.8	26.8	16.8
CdO	.089	.118	.012	.113	.087	.109	.129	.129	.139
SLAG									
ZnO	.001	.001	.001	.001	.001	.001	.001	.002	.001
PbO	.001	.001	.001	.001	.001	.001	.002	.001	.002
FeO	7.79	4.34	7.65	3.95	3.78	7.45	7.53	5.46	3.70
CdO	.002	.002	.002	.002	.002	.002	.001	.001	.001
METAL									
Zn	.002	.001	.002	.002	.002	.001	.001	.002	.002
Pb	.002	.008	.001	.001	.001	.001	.001	.002	.001
Cd	.002	.002	.001	.002	.002	.002	.001	.001	.002

Table 2-D: Recovery of Zn, Pb and Cd in Dusts Collected at the LB Furnace, %.

RUN # ELEMENT	1	2	3	4	5	6	7	8	9
Zn	72.9	76.9	90.0	70.5	84.4	70.8	85.6	73.8	78.5
Pb	55.8	62.0	50.6	65.3	86.0	95.5	96.5	83.9	94.1
Cd	64.6	36.9	98.5	49.3	52.1	66.7	66.5	52.3	56.7

Table 3: Experimental Results with Medium and High Zinc EAF Dusts.

RUN #	11	12	13	14	15	16	17	21	22

Composition of Reacting Mixture, % Wt.

DUST	EAF 2							EAF 3	
	37.2	37.2	37.2	37.2	54.0	54.0	72.0	38.0	38.0
Mill Scale	37.2	37.2	37.2	37.2	20.0	20.0	–	38.0	38.0
Coal	18.6	18.6	18.6	18.6	20.0	20.0	20.0	20.0	20.0
Glass Scrap	7.0	7.0	7.0	7.0	6.0	6.0	3.0	–	–
Sand	–	–	–	–	–	–	5.0	4.0	5.0

Chemical Composition of Reaction Products, %Wt.

BAGHOUSE DUST									
ZnO	44.3	39.9	47.3	41.3	54.6	57.8	58.9	59.4	52.9
PbO	10.2	8.0	5.0	6.9	9.1	8.8	11.6	10.1	9.9
FeO	22.6	19.9	20.9	23.1	7.3	5.5	9.9	17.6	9.6
CdO	0.16	0.29	0.13	0.13	0.13	0.12	0.09	0.10	0.10
FeO in Slag	2.9	2.2	2.3	3.5	2.1	2.3	0.87	6.0	4.3

Recovery of Zn, Pb and Cd in LB Dust, %.

Zn	60.0	59.4	70.8	57.7	68.9	84.3	67.0	75.9	66.3
Pb	90.2	82.9	59.7	70.4	76.0	88.9	97.4	73.5	49.0
Cd	69.5	98.7	76.2	71.9	39.8	51.1	64.6	90.1	81.0

Table 4: Experimental Results with BOF Dusts.

RUN #	31	32	33	34	35

Composition of Reacting Mixture, % Wt.

BOF DUST	37.0	35.5	38.0	38.0	80.0
Mill Scale	37.0	36.3	39.0	39.0	-
Coal	19.0	21.4	23.0	23.0	20.0
Sand	7.0	6.8	7.0	7.0	14.0

Chemical Composition of Reaction Products, %Wt.

BAGHOUSE DUST					
ZnO	36.9	30.9	28.7	29.8	34.8
PbO	8.93	8.10	5.95	7.10	9.94
FeO	36.9	33.8	12.7	29.8	30.7
CdO	0.09	0.08	0.08	0.07	0.001
FeO in Slag	6.1	4.8	4.1	4.9	21.1

Recovery of Zn, Pb and Cd in LB Dust, %.

Zn	97.1	94.3	97.2	94.7	82.7
Pb	56.0	60.6	45.8	43.9	49.5
Cd	68.0	72.1	64.3	70.2	-

Table 5: Experimental Results with Slag of Secondary Lead Smelting.

RUN #	41	42	43	44

Composition of Reacting Mixture, % Wt.

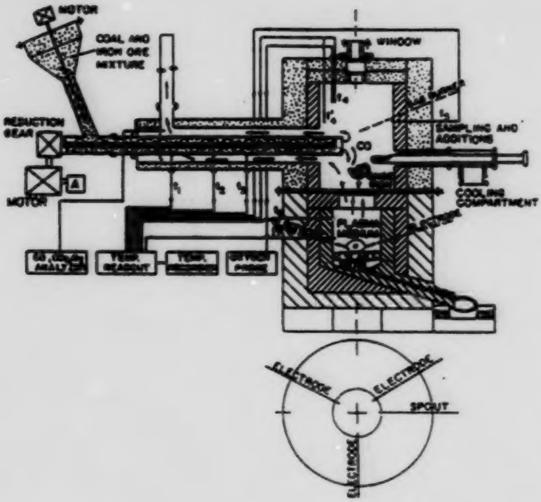
Lead Slag	83	83	79	77
Coal	17	17	21	23
Lime	-	-	4.5	4.5

Chemical Composition of Reaction Products, %Wt.

BAGHOUSE DUST				
ZnO	13.2	13.4	5.37	7.17
PbO	26.6	26.2	54.3	30.3
FeO	38.6	30.3	14.0	24.6
CdO	0.02	0.02	0.002	0.001
FeO in Slag	16.4	14.2	2.14	5.54

Recovery of Zn, Pb and Cd in LB Dust, %.

Zn	99.2	95.6	82.0	122
Pb	29.2	26.4	59.5	37.1
Cd	44.0	40.2	-	-


MOTOR
COAL AND IRON ORE MIXTURE
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SAMPLING AND ADDITIONS
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Fig. 1: Cross-Section of the Bench-Scale LB Furnace.

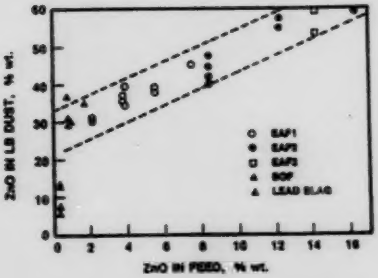

Fig. 2: ZnO in the Feed vs. ZnO in LB Furnace Dust.

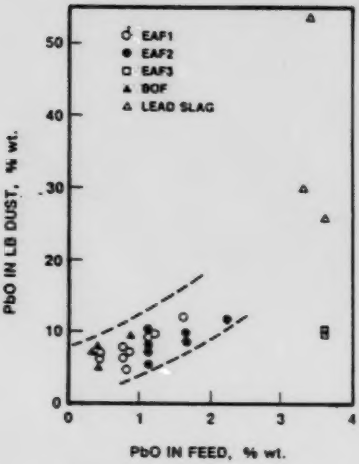

Fig. 3: PbO in the Feed vs. PbO in LB Furnace Dust.

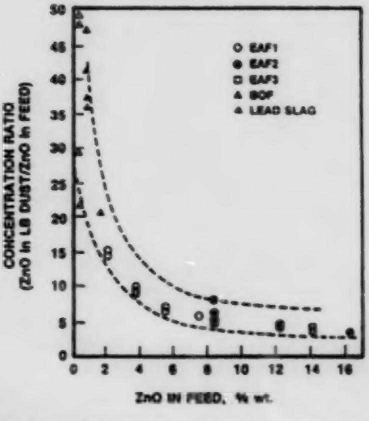

Fig. 4: Enrichment of ZnO Oxide in LB Furnace Treatment

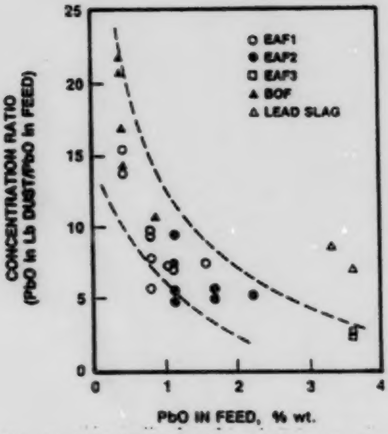

Fig. 5: Enrichment of PbO oxide in LB Furnace Treatment.

C12

In Situ* Biodegradation of Chlorinated Solvents. D.W. Major* and E.W. Hodgins, Contaminant Hydrogeology Services, Beak Consultants Limited, Guelph, Ontario, N1H 3Y5

Chlorinated ethenes, such as tetrachloroethene and trichloroethene, are dense, non-aqueous solvents which have solubilities 3 orders of magnitude greater than their respective drinking water limits. Their physical properties and their ubiquity in manufacturing and service shops have led to these compound being one of the most frequently encountered groundwater contaminants. PCE can be sequentially dechlorinated anaerobically to form vinyl chloride (VC), which is an undesirable end-product. A field investigation at a chemical transfer facility indicated that PCE had entered subsurface and had contaminated the groundwater. What was interesting is that the extent of VC distribution was not as great as would be expected if it was persisting in the groundwater. The objective of our research was to gain insight into the possible microbial processes that may be responsible for the degradation of tetrachloroethylene (PCE) and its degradation products, particularly VC. Our initial field study has indicated that methanol (stored at the facility) and acetate were present in the groundwater. Methanol may be promoting the degradation of PCE past VC, whereas, acetate may promote the formation of VC. This conclusion is based upon the ratio of VC/PCE or VC/TCE in monitoring wells as compared to the presence or absence of methanol or acetate. The presence of ethene and ethane in groundwater samples may imply the degradation of VC by undergoing another reductive dehalogenation step forming ethene (which may be further undergo the equivalent of catalytic hydrogenation to form ethane). Gossett and Freedman (1989) have shown in laboratory studies that methanol promotes the degradation of PCE and TCE to ethylene gas under methanogenic conditions. The detection of ethene at our site provides collaborative field evidence of laboratory results indicating that complete dechlorination of PCE and TCE can occur and be environmentally significant. Acetate is an interesting co-contaminant at the site. It is possible that acetogens are forming acetate from the metabolism of methanol. The high concentration of acetate in samples from one groundwater well, which had highest concentration of methanol, supports this possibility. Current work is focusing on characterizing the microbial community using classical microbiological techniques and lipid analysis of authentic core material from the site. Microcosms experiments are evaluating the effect of methanol and acetate on the degradation of PCE. Future work entails the use of *in situ* test columns for controlled field experiments aimed at selectively inducing microbial populations to degrade PCE and VC.

C13

CLASSIFICATION AND LEACHABILITY OF HAZARDOUS WASTES AND HAZARDOUS WASTE RESIDUES.

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In work reported at the 1989 Technology Transfer Conference, it was shown that the non-volatile heavy metals present in waste residues such as sludges and incinerator and furnace ashes could be successfully immobilized in a waste form based on a soda-lime glass. When subjected to the Regulation 309 Leachate Extraction Procedure, the release of heavy metals lay between 3 and 4 orders of magnitude below that from the raw waste. When subjected to serial leaching tests, the releases of heavy metals were below chemical detection limits, but release rates of ~1 x 10^{-9} g/cm^2·d were inferred from radioactive tracer experiments.

In a climate of increasing regulatory scrutiny, it will become necessary not only to demonstrate that current releases of heavy metals from disposed waste forms into the environment are acceptably low, but also that there is a sound basis for projecting these release rates into the future. This paper outlines the development of theoretical models that describe release from glassy waste forms, together with preliminary results from experiments designed to verify the models.

C14

NON-LINEAR SORPTION OF PHENOL ON NATURAL CLAY AND ITS INFLUENCE ON DIFFUSIVE MIGRATION

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ABSTRACT

Phenol (C_6H_5OH) sorption onto soil solids is shown by batch testing to be a non-linear function of pore water concentration, with much greater sorption at low concentrations. This results in K_d values ranging from 3 mL/g at low concentrations (~ 0.5 mg/L) down to 0.5 mL/g at high concentrations (~ 100 mg/L). As a consequence of non-linear sorption, the magnitude of the source concentration can affect the rate and distance of solute migration, a feature not observed for constant K_d. Simulated profiles using POLLUTE are presented to demonstrate the significance of the batch test observations.

INTRODUCTION

Disposal of solid wastes to land has been the most prevalent means of disposal in the past and, it appears, will remain so well into the foreseeable future. The growing interest in and practice of recycling and the development of new waste processing techniques may alter the quantity and nature of the waste, but a residue requiring disposal will inevitably remain.

Phenol is a common constituent of municipal landfill leachates typically at concentrations of ~ 5000 µg/L which is several orders of magnitude higher than the Ontario Ministry of the Environment's drinking water maximum of 2 µg/L. It is also widely used in the synthesis of many industrial chemicals and is generated as a waste product from numerous industries and, thus, finds itself in numerous industrial landfill leachates. It is moderately toxic to humans and causes disagreeable odours in drinking water at very low concentrations. The U.S. E.P.A. has classified phenol as a priority pollutant.

The driving processes in the migration of phenol in soil are advection and diffusion, modified by attenuating processes of adsorption, and chemical and biochemical degradation. This paper presents the results of sorption tests conducted with phenol in aqueous solution and examines the potential implications of the observed sorption characteristics.

THEORY AND BACKGROUND

Sorption is a term used to describe the process of solute removal from solutions by soil solids. It includes both adsorption, the transfer of solute to the surface of soil solids, and absorption, the transfer of solute to the matrix of soil solids. For soils containing solids such as organic matter, adsorption would normally be expected to be much more dominant than absorption.

One method for determining the degree to which a solute will sorb to soil solids is batch testing. In batch tests a known mass of soil is shaken as a slurry with a known volume of solution containing a known concentration of the solute of interest. After a period of time (hours to days) the degree of partitioning is determined by measuring the change in solution concentration. Batch test results are "optimum" sorption values since the exposure of the sorbate (the solute) to the sorbent (the soil) is maximized by mixing.

To describe the equilibrium relationship between mass of solute sorbed per unit mass of soil to the concentration of solute remaining in the liquid phase, the equilibrium equation or isotherm commonly used in soil systems is the Freundlich Isotherm. It has the form:

$$[1] \qquad x/m = KC^{1/n}$$

where x is the mass of solute sorbed on the soil, m is the mass of soil, K is a constant indicative of sorptive capacity (Zytner et al., 1989), C is the solution concentration after sorption, and 1/n is a constant indicative of sorption intensity (Zytner et al., 1989).

The constants shown in [1] are determined by plotting the mass sorbed versus the equilibrium concentration on double logarithmic paper. Typically, a log-linear distribution of the data points results from which K is obtained from the intercept and 1/n is obtained from the slope of the curve.

The distribution or partitioning coefficient, K_d, is commonly used to describe the partitioning of the solute between the liquid and solid phases. It is taken from the slope of the isotherm:

$$[2] \qquad K_d = \frac{d(x/m)}{dC} = \frac{d(KC^{1/n})}{dC}.$$

If 1/n equals 1 then the isotherm will also plot linearly in arithmetic space and the magnitude of K_d will equal K. The linear distribution coefficient has been widely used to describe the sorption of organics on soil (Karickhoff et al., 1979; Banerji et al., 1986; Zytner et al., 1989; Johnson et al., 1989). And although some authors have noted the fact that 1/n can be significantly less than 1, apparently there has been little or no study of the consequences of assuming linear sorption.

Johnson et al. (1989) observed "highly non-linear sorption isotherms" for the hydrophobic organic compounds trichloroethene, benzene, toluene, and ethylbenzene in aqueous concentrations between 0.1 and 25 mg/L in Sarnia area clayey soils. However, they chose to represent sorption in terms of a linear K_d, based on batch sorption experimental data conducted at solution concentrations of ~ 1 mg/L. The batch test experimental data were not presented with the paper. Similarly, Banerji et al. (1986) reported non-linear sorption of pentachlorophenol on soils but chose to present a linear K_d. They state that "most contaminant models treat adsorption as a linear function because of difficulties a non-linear adsorption term creates in solving the governing differential equation".

This paper presents the results of 24-hour batch tests on "unmodified" soil-phenol solution mixtures with the partitioning coefficient, K_d, determined using the Freundlich equation. "Unmodified" means that the physical and chemical characteristics of the soil and slurry were not altered by the addition of chemicals or removal of constituents. Since different soils may have different adsorption equilibrium times due to differing physical properties such as the organic carbon content and surface area (Zytner et al., 1989), kinetics tests were performed to evaluate the validity of the 24-hour testing time.

MATERIALS AND METHODS

A sample of clayey soil from 7 metres depth in a background borehole at the LaSalle Road industrial waste landfill site was air dried, pulverized and well mixed to ensure representative subsampling. The x-ray powder patterns and the traces for oriented fines indicated abundant quartz, carbonate, illite and chlorite, moderate amounts of feldspar and a trace of smectite. The fraction of organic carbon, determined using a modified Walkley-Black technique (Allison, 1965) was 0.78%.

Masses of the air dried soil were mixed with aqueous solutions of phenol in 25 mL Corex glass centrifuge tubes with Teflon-lined seals held in place by plastic screw caps. The mixtures were shaken with a "wrist action" shaker in the absence of light at laboratory temperatures (~ 23°C). Equilibrium phenol solution concentrations ranged from 100 mg/L to 0.5 mg/L. Ratios of the mass of soil to the mass of aqueous phenol solution ranged from 0.02 to 1.6. These ratios are significantly lower than natural in situ ratios, which are typically 4 to 5. Thus, the degree of sorption was optimized in the batch tests by having large solution volumes.

After 24 hours, the tubes were centrifuged to separate the soil from the solution and the amount of phenol solute remaining in aqueous solution was determined by gas chromatography. The difference between the initial and final equilibrium concentration was designated as being sorbed by the soil.

RESULTS

The sorption of phenol on this soil is described by the Freundlich isotherm with constants, $K = 2.0$ to 3.3 and $1/n = 0.628$ when C is in units of mg/L and x/m is in units of mg phenol per kg dry soil. Because 1/n is not close to unity the isotherm should not be taken as linear. Thus, the sorption coefficient, K_d, does not have a unique value for all equilibrium concentrations, C, and is described by:

[3] $$K_d = 1.256 \cdot C^{-0.372} \text{ to } 2.682 \cdot C^{-0.372}.$$

This relationship is shown graphically on Figure 1.

Because phenol dissolves almost exclusively in molecular rather than ionic form, the ion exchange sites of charged clay minerals probably are not significant sorption sites. Various authors (Hamaker and Thompson, 1972; O'Connor and Connolly, 1980; Morrill et al., 1982; Voice et al., 1983; and Zytner et al., 1989) cite soil organic matter as the principal sorption sites for dissolved organic molecules. Phenol is also considered to sorb mainly at organic sites. Many authors normalize the sorption of organics with the fraction of organic carbon as described by Karickhoff et al. (1979). The resultant organic carbon distribution coefficient, K_{oc}, for phenol is:

[4] $$K_{oc} = \frac{K_d}{f_{oc}} = 161 \cdot C^{-0.372} \text{ to } 344 \cdot C^{-0.372}.$$

DISCUSSION

Linear isotherms suggest that the sorption of a solute on a soil increases indefinitely with the concentration of solute, independent of the mass of sorbent. Clearly, an infinite number of sorption sites are not available in a finite mass of sorbent. Thus, at a sufficiently high concentration even a linear isotherm must deviate from its linear trend, eventually levelling off when all sorption sites are satisfied. The range of concentrations over which sorption may appear linear will depend on the solute characteristics and the nature of the sorption sites.

Since e phenol sorption constant $1/n$ is considerably less than one, a greater proportion of solute is sorbed from lower concentration than higher concentration solutions. For example, from Figure 1, when $K = 2.5$ the equivalent linear values of K_d for equilibrium solutions of 30 and 3 mg/L, respectively, are 0.44 and 1.04 mL/g.

The non-linearity of the isotherms implies that, unlike species that sorb linearly, the extent of migration of a dissolved species at any given time will be dependent on the magnitude (and history) of the source concentration. To illustrate this, an updated version of POLLUTE (Rowe and Booker, 1990) was used to generate C/C_o plots vs depth for three different source concentrations, C_o, of 1, 5 and 50 mg/L (Figure 2). The three dashed profiles for $t = 20$ annum yield increasing depths of migration as C_o increases from 1 to 50 mg/L. For all three curves $K = 2.5$ which means K_d decreased from ~ 1.7 to ~ 0.4 with increasing C_o. For assumed linear adsorption with $K_d = 2.5$, the solid C/C_o profile is generated for all values of C_o at $t = 20$ a. It is clear from comparison to the dashed curves that this assumption does not model phenol very satisfactorily.

Actual field profiles for phenol are available for the LaSalle Road landfill, however, they are severely elbowed which means other processes such as biodegradation may be operative (Mucklow, 1990). These curves will be shown as part of the oral presentation.

CONCLUSIONS

Batch tests were conducted using aqueous phenol solutions mixed with natural clayey soil. The major conclusions are as follows:

1. The sorption of phenol on this natural clayey soil is a non-linear function of the porewater concentration, resulting in K_d values as high as 3 mL/g and as low as 0.5 mL/g as the equilibrium solution concentration was varied from 0.5 mg/L to 100 mg/L.

2. Use of non-linear isotherms when modelling diffusion profiles should result in better predictions of the distance of phenol migration.

ACKNOWLEDGEMENTS

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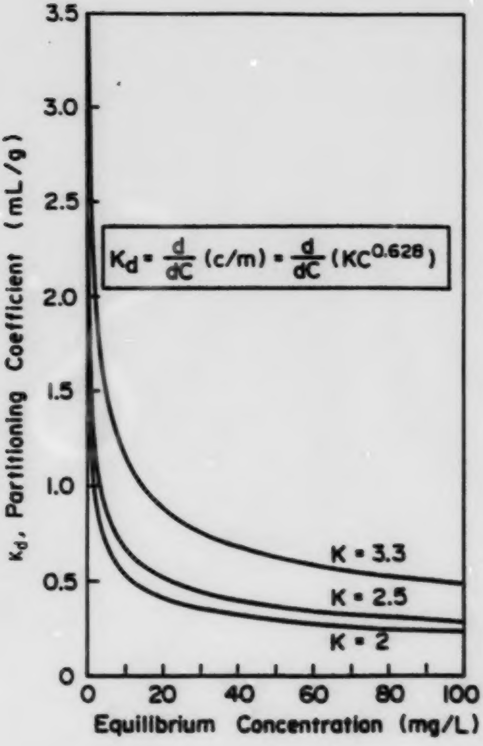

FIGURE 1. PHENOL PARTITIONING COEFFICIENT, K_d

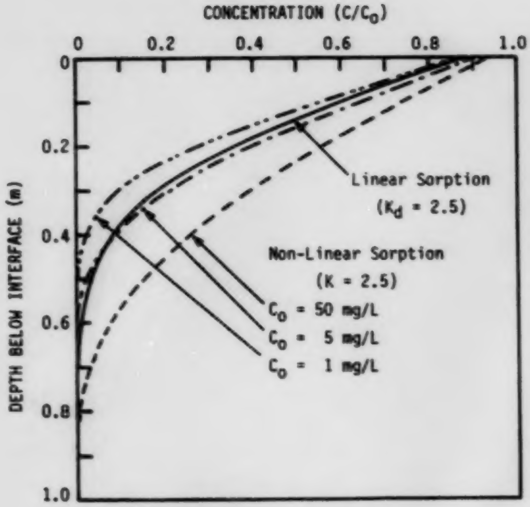

FIGURE 2. RELATIVE CONCENTRATION PROFILES GENERATED BY POLLUTE TO COMPARE EFFECTS OF LINEAR AND NON-LINEAR SORPTION

Test Conditions: $D = 5.3 \times 10^{-6}$ cm^2/s; $n = .38$;
$\rho_d = 1.713$ g/cm^3; $t = 20$a; $H_\ell = 7$ m;
$C_{background} = 0$

Boundary Conditions: Upper → Finite Mass of Contaminants;
Lower → Infinite Bottom Layer

Estimating Landfill Leachate and Contaminant Production

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ABSTRACT

In a landfill, the start of leachate production and contaminant release does not wait until the last green garbage bag has been delivered. It begins the day the first one arrives. It does not remain constant in time nor is it the same for all areas of the site.

The purpose for the work was to develop a rational means for estimating the variable contaminant production that occurs within a landfill throughout its entire life. Discerning the leaching history of one area from that of another was the goal of the research.

The 'Contaminant Estimation in Landfill Leachate' (CELL) model was developed for this purpose. It employs contaminant release curves which calculate the mass of contaminant released as a function of the volume of leachate passing per unit mass of waste.

Estimates of leachate flows used in the CELL model were generated using a modified version of the HELP model developed in this research. This modified method predicts an earlier first appearance of leachate than does the standard application of the model. The rate of site construction and precipitation determine when it appears. Tests using hypothetical landfills indicated that the modified HELP model can be applied successfully to both the construction period and the post closure period of a landfill.

The estimate of contaminant production using the CELL model compared well in both magnitude and pattern with the general trends observed in the field. The model should be upgraded to consider the variability in the initial amounts of contaminants in the waste.

INTRODUCTION

In a landfill, the start of leachate production and contaminant release does not wait until the last green garbage bag has been delivered. It begins the day the first one arrives. The production and contamination of the leachate that begins during the early stages of landfill construction continues for many decades beyond the closure date. Both the leachate quantity and quality produced over this period are dependent on many factors and recently, efforts have been made to model the leaching process.

In current landfill design practice, the computer programs used for estimating the quantity of leachate produced do not include the time it takes to build the landfill up to final cover in the time frame of the simulation. The simulation period generally starts from the time the landfill is near completion. As a result, the leachate production occurring during construction cannot be estimated. Furthermore, the leaching history during this period determines the initial conditions of the landfill which are needed as input for the start of the computer simulations.

The production of contaminant is similar to leachate quantity in that contaminant production occurs during the entire life of the site. However in terms of computer models there are no acceptable models available to simulate contaminant production over this period. The original impetus for the study was to develop such a model, a leachate quality model, but it was soon realized that estimates of the quantity of leachate produced during construction were needed first. The reason for this is that the controlling variable for the proposed contaminant release model was the volume of liquid passing through the waste. This concept is a continuation of work done by McGinley and Kmet (1984), Farquhar (1987) and Reitzel (1990).

This paper focuses on the methods developed for estimating leachate quantity during construction and post closure periods. An introduction to the aspect of leachate quality is also included. A second paper covers the leachate quality problem in more detail.(Jarvis & Farquhar 1990)

THE HELP MODEL

The Hydrologic Evaluation of Landfill Performance (HELP) Model is the latest development in the short series of models for solid waste landfill simulation.(Schroeder et al. 1984) It represents an attempt to model many of the hydrologic phenomena that take place in and above an landfill all in one package. The HELP model is currently the best of the models available for landfill simulation. At this point it should be noted that the model uses English units and therefore, the results for this study are also presented in English units.

The start of a standard simulation is typically at the point when the final refuse height has been reached and/or when the final cover layer is complete. Figure 1a illustrates the growth of a landfill. The last three stages indicated by the letters B, C and D are the points at which the HELP model can be used to simulate leachate production. Figure 1b is a graphical sketch of what the corresponding leachate production curve might look like from each of the three simulations.

Figure 1a Stages of Landfill Construction

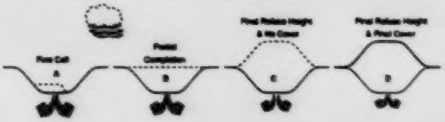
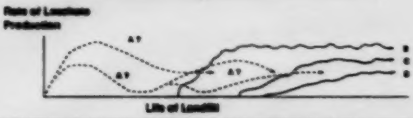

First Cell
A
Partial Completion
B
Final Refuse Height & No Cover
C
Final Refuse Height & Final Cover
D

Figure 1b Representative Leachate Flows From Model Simulations At Different Stages of Landfill Construction



The differences between the curve show the effect of such large time increments between simulation. It is possible to simulate a site at any refuse depth, but long term simulations of sites that have a majority of the waste in place are most common. The main reason for this is that the HELP model algorithm is not designed to simulate the changing dimensions of the landfill during construction. Also, landfill designers are often interested in long term steady-state leachate production for the purpose of comparing different design alternatives.

There are two shortcomings associated with this gap in the simulation period, the first one has an important influence on the second. The shortcomings are:

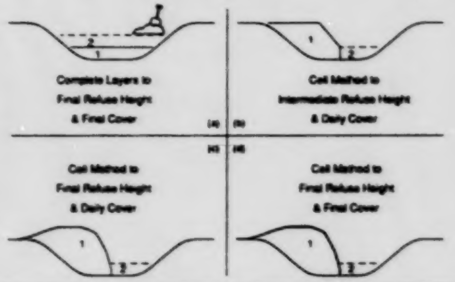
1) a significant amount of the early leachate production is not accounted for and,

2) the amount of contaminant released during this period cannot be identified without knowing the amount of leachate flowing through the waste.

This first point is important because leaching occurs during this early period when the waste is exposed to direct precipitation, the runoff is low and the waste depth is shallow. This period is represented as stage A on Figure 1. The manner in which the landfill is constructed in going from stage A to B affects the amount and rate of leachate production which are illustrated by the dotted lines in Figure 1b. Each of these three dotted curves represents a different method of landfill construction.

Figure 2 highlights the different methods of landfill construction which have a direct impact on the rate and amount of leachate production. The first landfill, Figure 2a, shows the landfill being constructed layers until the final refuse height is reached. Each layer covers the entire area of the site. The remaining landfills use the cell method of construction. In Figures 2b and 2c, the refuse is placed in a section of the landfill up to the final height. Subsequent waste is then placed in adjacent areas in a similar manner. Figure 2d represents the case in which the waste is constructed to some intermediate height after which construction continues in an adjacent cell.

Figure 2 Methods of Landfill Construction



The amount of leachate produced over this early stage determines the amount of contaminant released or conversely the amount of contaminant remaining. It is important to know the leaching potential of the waste at different times for the design of efficient leachate treatment facilities. Therefore, the estimates of leachate flow generated in a standard HELP simulation are not adequate for estimating the release of contaminants in a landfill at any point in its life.

The major part of this research consisted of modifying the HELP model to simulate the construction of a municipal solid waste (MSW) landfill. Furthermore, the results of this new method would be compared to standard simulations and to trends in leachate production found in practice. For example, the first leachate from a landfill appears sooner than predicted by the HELP model and thus, the intention was to modify the model to account for this.

HELP MODEL MODIFICATIONS

A standard HELP model simulation of a landfill requires information from three categories, they are: climatologic data, design specifications and soil characteristics. Rather than redesign the entire HELP model, the approach taken was to divide the entire landfill into small areas for simulation and to modify the input data for each of these areas. The following summarizes the main ideas behind the method. A detailed explanation of the procedure can be found elsewhere.(Jarvis 1989).

1 DESIGN SPECIFICATIONS

For each area of a site to be modelled, a series of short simulations are performed; each one in the series spans a discrete time interval in the construction of the landfill. The results of all these short simulations are linked together to form the complete leachate production history.

The design specifications for each simulation can be thought of as a numerical snapshot of the waste in time as the area is being constructed. The only difference between the snapshots is the depth and moisture content of the waste.

2 WASTE AND SOIL CHARACTERISTICS

In order to link the results of these simulations together, a modification of the HELP model was required to ensure continuity in the water budget from one simulation to the next. Typically, at the start of the simulation the moisture content of each layer (soil and waste) are initialized to a value which is either specified by the user or set to default values by the program. At the start of the simulations for the modified approach, the initial moisture contents of the lower soil and waste layers must be set equal to their respective final values at the end of previous simulation. The HELP model code was edited to output the soil moisture levels at the end of each simulation period.

3 COMBINING THE RESULTS

The final modification of the HELP model involved editing the code to generate a separate file for the leachate flow values alone. One point should be clarified here. The HELP model divides the leachate flow at the base of the landfill into lateral drainage and vertical percolation through the liner. The code was modified to recombine these two flows so the total amount of leachate exiting the waste itself is output into a file. This combined value was needed for the calculations of contaminant production.

AN EXAMPLE LANDFILL

To illustrate the above modifications of the HELP model, an simple landfill example was developed. Although the precipitation, landfill geometry and type of construction for the hypothetical case has been simplified, the method can be applied to any situation.

1 THE SITE

A small landfill was comprised of three 4m waste layers which required four months each for placement; placement of the first layer began in January 1990, the second in May 1990 and the third in September 1990. This scenario represents the construction of waste to an intermediate height after which, the incoming waste is deposited in an adjacent area starting at ground level.(Figure 2b)

The first analysis of the site used the conventional application of the HELP model with all three layers in place in September 1990. The simulation was run from September 1990 for five years to the end of 1995. This is a typical application of the HELP model.

The second analysis used the modified form of the model. The simulation period was extended to include the initial construction period from January to September. In both cases, the site remained open (no final cover) for the entire simulation period. Furthermore, because the site was open, no runoff was permitted from the site.

The precipitation data used for both cases was a simplified three phase cycle repeated for each year of the simulation. The first phase extended from February to May with an average of 7.5 in./month (190 mm/month), the second phase from June to September with an average of 1.2 in./month (30 mm/month) and the last phase from October to January with an average of 3.9 in./month (100 mm/month).

2 MODIFIED HELP SIMULATIONS

For the second analysis using the modified HELP model, three simulations were required for the construction period; each one spanned the time period that each of the three layers was exposed (prior to being covered by the next waste layer). Defining the limits for these periods was difficult. The actual placement of the refuse is a continuum of activity; each lift takes time to grow to completion and is not instantly covered when the next layer is started. Some limit had to be decided upon as to how many simulations would be used to model the growth of the waste. Thus, it was assumed that the entire depth of waste for each lift was placed instantaneously for the start of the simulation period.

The results of the three simulations are in the form of three leachate flow profiles. These four month segments of leachate flows were linked in sequence to form the leachate profile for the entire first year of the construction.

3 INITIAL CONDITIONS

Standard Simulation

For the first analysis which used the standard application of the HELP model, the initial soil moisture condition for all three of the waste layers was set equal to 0.2754 (vol./vol.). This is the default value for a standard HELP model application.

Modified Simulation

For the second analysis only the topmost layer was assigned the default initial soil moisture content. The default value was used for the purpose of comparison in this research. Further work should look at the season the layer was placed and adjust the content accordingly. For example, if a layer was constructed during the spring, a slightly higher initial soil moisture would be expected.

Therefore, for the first simulation, the first layer started with an initial soil moisture contents of 0.2754 (vol./vol.). At the start of the next simulation in May, the initial moisture content of this first layer was changed to the value output for the layer in April and the initial moisture content of the second (new) layer was set to the default value.

This process was repeated for the third simulation. The last step was to continue the simulation for an additional five years to the end of 1995. At the start of this final simulation the soil moisture contents for the three layers were adjusted to their respective values at the end of December 1990 to maintain the water budget balance.

4 RESULTS FOR THREE LAYERS

The results of these two analyses are shown in Figure 3. Leachate first appears earlier with modified approach than it does with the conventional application. In the modified approach, the first significant amount of leachate appears in March 1990 whereas in the standard application it does not begin until the latter half of 1991. This is consistent with field observations.

5 EXTENDING TO NINE LAYERS

The second step in this investigation was to repeat these two analyses on a section where the construction continued to final refuse height.(Figure 2c) Rather than stop at three layers the site was extended to nine layers which took three years to construct. Again, the first layer was placed in January 1990 but the final layer was not place until September 1992. Therefore, in the standard application of the model, the simulation began in September 1992 and was carried out to the end of 1999. In the modified analyses, the simulation period covered the first three years of construction and extended for a period of seven years past construction to the end of 1999.

Figure 3 Monthly Leachate Production From Three Layers of Waste With Initial Moisture Content = 0.2754

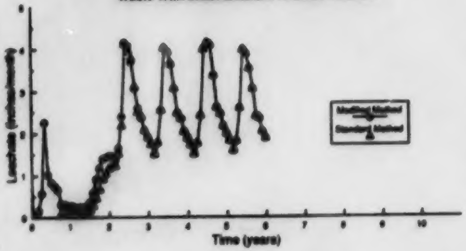


Figure 4 Monthly Leachate Production From Nine Layers of Waste With Initial Moisture Content = 0.2754

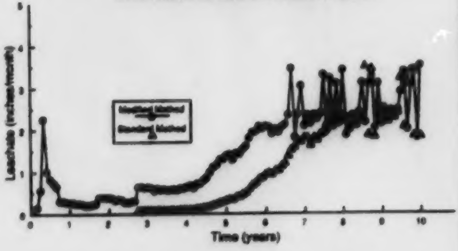


Figure 5 Cumulative Leachate Production From Nine Layers Using 2 Methods & 2 Initial Moisture Contents

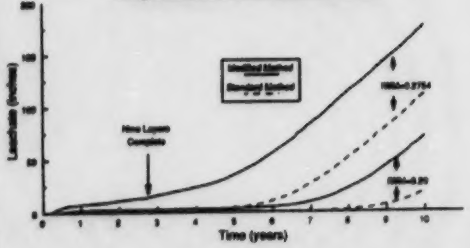
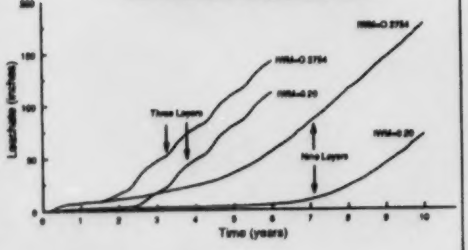


Figure 6 Cumulative Leachate Production From Three & Nine Layers Using Modified Method



The same precipitation cycle that was used for the three layer study was used in this part of study. Also, the depth of the layers remained at 4 m and the same pattern was used for constructing the waste; January to April, May to September and October to December.

The results of the two analyses on the nine layer test site are presented in Figure 4. The diagram shows the leachate production resulting from the two approaches to modelling the waste layers. In the standard case, significant leachate production did not begin until the end of 1994. Steady-state production, fluctuating seasonally but averaging approximately 3 in./month, was achieved in 1998.

For the modified approach, leachate first appeared within the first year (1990) for a short period and continued throughout the construction period at a rate of approximately 0.5 inches/month. Leachate production began to increase steadily once all the layers were in place (end of year three). Steady-state production (approximately 3 in./month) was achieved at the end of 1996, two years earlier than the standard case.

Figure 5 shows the cumulative leachate production for the two cases (top two lines). By the time the standard simulation was started, the modified case had predicted approximately 20 inches of leachate production. By the end of 1995 the modified method had estimated 50 inches more leachate than the standard method and 70 inches more by the end of the tenth year. Because both cases had achieved steady-state at the end of the ten years, this difference of 70 inches would stay constant. However, the difference between contaminant concentrations would not be.

In all cases, the final steady-state rate of leachate production would be reduced if a final cover were constructed.

6 EFFECT OF DRY WASTE

The examine the effect of dryer waste layers, the above simulations were repeated with the default value of 0.2754 (vol./vol.) for the initial waste moisture (IWM) content lowered to 0.20 (vol./vol.). Again, in the modified cases only the top layer was assigned this value; the values for the lower layers were assigned the correct values to maintain the water budget. For the standard application, all the layers were assigned the initial moisture content of 0.20 (vol.vol.).

As expected, the early rate of leachate production was lower for the dryer waste scenario. Figure 5 shows the cumulative leachate production for the two methods for both the high and low IWM contents. In both cases, the modified method produced more leachate than the standard case at each level of initial moisture content. Even the modified method at low initial moisture predicted approximately 2 inches of leachate production before the standard method even started.

7 IMPACT OF DIFFERENT CONSTRUCTION METHODS

The effect of different methods of construction is evident in the comparison of the results of leachate production in the first five years for the three and nine layer cases. The three layer case represents lateral construction; the three layers are placed and then construction begins again at ground level in an adjacent area. The nine layers represents vertical construction toward final refuse height.

Figure 6 represents the cumulative leachate production for the three and nine layer cases at the two levels of initial moisture contents. As expected, for a given initial moisture content the open three layers produced more leachate by the end of the first five years than did the nine layer case. In the nine layer case, more of the infiltration was diverted to saturating the rapidly growing column of waste. Thus, vertical construction is preferable for reducing total leachate production.

Prior to the end of year three, the leachate production for the nine layer-high IWM case exceeds that of the three layer-low IWM case. Beyond this point, the opposite holds true. This illustrates how the rate of vertical construction can affect the rate of leachate production. If the nine layers were placed at a slower rate, each layer would have more time to become saturated and the entire column would reach steady-state earlier. The result on the graph would be that the nine layers-high IWM curve would approach a shape similar to the shape of the three layers-low IWM curve. From these results, it is the case that, for a given rainfall rate, both the rate of vertical construction and the initial waste moisture determine the profile of the leachate production.

Finally, the graph also illustrates how the additional layers damp out the effect of the seasonality in precipitation on the production of leachate. The seasonal fluctuations are more evident in the three layer case.

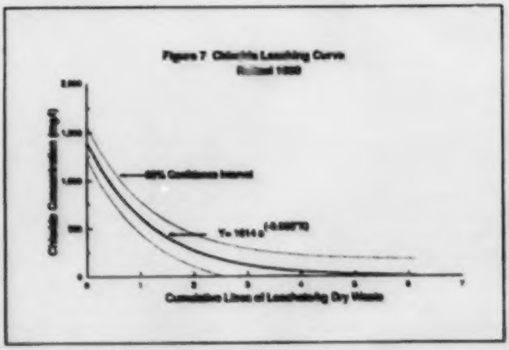
In this simplified case, the results are expected. However, in reality the possibility that each layer has a different initial moisture content explains the highly variable nature of the early leachate production. This could be modelled by assigning initial moisture contents according to the season in which the waste was deposited.

CONTAMINANT PRODUCTION

In recent years, attempts have been made to characterize the quality of leachate based on a number of independent variables. The most common has been the age of the waste.(Wigh 1984, Lu et al. 1984) The difficulty with using the age of the waste is that, for 20 year old waste for example, the remaining leaching potential of the waste is considered to be the same regardless of whether it is located in a dry climate or in a wet climate.

More recently, research by McGinley & Kmet (1984), Farquhar (1987) and Reitzel (1990) has investigated the leachate quality as a function of the volume of liquid passing through the waste. It can be thought of as a rinsing effect. Thus, waste stored in a wet environment will have a higher contaminant production in the earlier years than will a waste which is stored in a dryer climate.

Figure 7 is an example of the curve developed for chloride in the research by Reitzel (1990); the equation for the curve is also given. The seven contaminants that were investigated included: chloride, nitrogen, phosphorous, iron, lead, cadmium and COD.



While this paper focuses on the research into leachate quality, subsequent work was carried out to incorporate the work of Reitzel (1990) into a model which will predict the leachate quality in a landfill. The model is called the 'Contaminant Estimation in Landfill Leachate' (CELL) model.(Jarvis 1989)

To give the reader an idea of the results of this work, the CELL model was applied to the example used to illustrate the leachate quantity research. Figure 8 shows the results for chloride and ammonia for the three layer site. Figure 8 also illustrates the effect of a dryer (IWM = 0.20 vol./vol.) and a wetter (IWM = 0.2754 vol.vol.) environment on the production of contaminant. In the wetter environment, more of the contaminant is flushed out of the waste earlier in time.

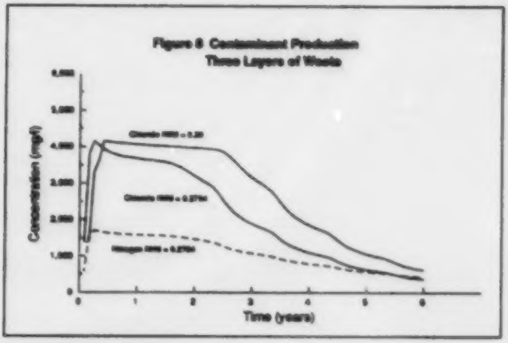


Figure 8 Contaminant Production
Three Layers of Waste

CONCLUSIONS

The results from this study indicate that, by modifying application of the HELP model to reflect the actual construction history of the waste, the resulting leachate patterns better reflect what is actually found in the field. Leachate production begins when the first layer is constructed and may or may not continue throughout construction depending on the other factors included in this study; type of construction, rate of construction and the initial waste moisture content.

The effect of different construction methods is that vertical construction, as opposed to lateral, reduces the total amount of leachate produced.

The analysis also revealed that the rate of vertical construction had an effect on the continuity of the production of leachate. The slower the layers are placed, relative to a fixed rainfall, the more likely a steady flow of leachate may continue from the time it first appears. The topmost layers have more time to reach field capacity by direct precipitation before a dryer layer covers them. A faster filling rate will result in a more fragmented flow profile and lower total leachate production.

The combined effect of the initial waste moisture content, fill rate and precipitation lead to the conclusions that there is no simple way to estimate the first appearance of leachate based on waste depth alone. Leachate flow can be reduced by rapid vertical landfill construction so that infiltration does not exceed the growth of in field capacity.

The introduction to the leachate quality at the end of this paper illustrates the impact of leachate quantity on leachate quality in a landfill environment. This information can assist in many areas such as the modelling of contaminant migration through a liner towards the groundwater and in the design of leachate treatment facilities.

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C18

Test of a Chemical Mechanical Process for the Decontamination of Non-Anatomical Biomedical Waste

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INTRODUCTION

Hospitals in the Metropolitan area produce an estimated 4.4 million pounds of yellow bag waste each year. Yellow bag hospital waste may consist of non-anatomical materials such as gauze, paper, swabs, plastics, syringes and needles, as well as lab cultures.

Studies have been initiated to examine methods of disposal of this biomedical waste; one process currently under investigation is the hammermill shredding/disinfection system. In the hammermill disinfection process the bags are coarsely shredded and concurrently sprayed with a solution of sodium hypochlorite. A high speed hammermill subsequently breaks the shredded waste into smaller particles. The wet mixture is then fed onto a perforated belt conveyor and the solid residue is dewatered before transportation to a disposal site. The liquid portion is separated for discharge into the municipal sanitary sewer.

The objective of this paper is to present an approach for evaluating the ability of the mechanical disinfection process to decontaminate biomedical waste. Emphasis will be placed on the following aspects of the evaluation: a) investigation of the effectiveness of disinfection using varying chlorine concentrations with different pH conditions and contact times; b) comparison of the inhibition of different species of the same bacterial genus by chlorine; c) development of a method for isolating viruses from untreated and treated hospital waste; d) comparison of desorption methods to recover bacteria that are adsorbed to crushed waste; and e) examination of the bactericidal activity of chlorine and Virkon on P. aeruginosa in crushed waste.

MATERIALS AND METHODS

Mechanical Crushers

The Medical Safe TEC Z-12, 500 Infectious Waste Disposal System grinds the waste to a granular size using a pre-shredder and a hammermill and simultaneously treats it with a disinfectant solution. The dry weight of the machine is approximately 4, 536 Kg.

The machine was not in operation when the study was initiated and therefore a smaller crusher, the Bio-Murbel 100, was used in the investigation.

The Bio-Murbel 100 Mechanical Waste Disinfecting and Disposal System uses a three blade crusher and mount system to grind materials such as glass, hard plastics, syringes and needles. A disinfectant is sprayed onto the material during the crushing of the waste. The dry weight of the machine is 100 Kg.

Disinfectants

The stock chlorine solution used as a disinfecting agent was 6% sodium hypochlorite. At the completion of each experiment, the chlorine was neutralized with sodium thiosulphate according to the reaction: $2Na_2S_2O_3 + Cl_2 \longrightarrow Na_2S_4O_6 + 2NaCl$.

The virucidal agent, Virkon™, was employed as a 2% solution. Since the neutralizing agent for Virkon has yet to be determined, the disinfectant was neutralized by dilution at the conclusion of each experiment.

Factors Affecting Chlorine Disinfection

The bactericidal effect of chlorine on *Pseudomonas aeruginosa*, *Serratia marcescens*, *Mycobacterium phlei*, *M. smegmatis*, *Bacillus subtilis* and *B. megaterium* was assessed using the methods described by Seyfried and Fraser (1980). Chlorine demand-free buffered water (CDFB) at pH 4.0, 5.0, 9.0 and 10.0 was used for all dilutions and assays. Glassware was acid washed, treated overnight with a 10mg/L sodium hypochlorite solution, rinsed with chlorine-demand-free water (APHA, 1989) and sterilized with hot air. The stock solution of approximately 10,000 mg/L free chlorine was kept refrigerated in the dark. The chlorine concentration was determined using the DPD colorimetric method (APHA, 1989).

The bacterial cultures were centrifuged and washed twice with CDFB adjusted to the appropriate pH. A 1.0 mL aliquot of culture and 1.0 mL of sodium hypochlorite (0.1 to 1000 mg/L) were added to 8 mL of CDFB. At time intervals of 1, 30, 60 and 120 min, 1 mL samples were removed and neutralized with sodium thiosulfate solution. Controls and test solutions were diluted and plated to determine the CFU/mL.

Elution of Viruses from Crushed Waste

The virus used was polio type 1, containing 100 $TCID_{50}$/0.1 mL (10^{-7}) with HBSS pH 7 as diluent. Freshly trysinised vero cells diluted in growth medium (1.3×10^6 cells/mL) and 24 h monolayers of vero cells in 24-well plates were the tissue cultures employed in the study. The washing/eluting agents included HBSS pH 7, HBSS pH9, Tryptose Phosphate Broth pH9, 3% Beef extract and 1% non-fat dry milk in 0.05 M glycine. The negative stain used for electron microscopy examination was 2% phosphotungstic acid.

Wash/elution Method

A 4g amount of sterile simulated crushed hospital waste was placed in each of three flasks and 40mL of the virus dilution was added. The flasks were left at room temperature with frequent, gentle agitation for 90 min. The fluid was then harvested and replaced with 40mL of one of the washing/eluting agents. After 5 min, with gentle agitation at 1 min intervals, these fluids were harvested, and, using sterile forceps, approximately one-tenth of the crush was removed and added to a tissue culture tube containing 4mL of the tissue culture cell suspension. The washes were repeated for a total of 10 times, using 40mL of fluid for each wash and harvesting a tenth of the crush with clean, sterile forceps after each wash.

Co-Cultivation Method for Testing for Presence of Virus on Crush

The harvested crush was added to 4mL of the cell suspension in tissue culture tubes. The tubes were incubated in a slanted position and examined daily. Within 24 h a monolayer of cells formed, with the subsequent appearance of a cytopathic effect within a few days if virus was present. Control tubes, containing untreated crush and the cell suspension were included. The monolayer formed within 24 h, but there was no cytopathic effect after further incubation.

Testing of the Washes

The ten washes collected from each of the washing/elution agents used were tested by inoculating 0.1mL of each into 4 cell monolayers in a 24 well plate. After 1 hr adsorption at 37°C, maintenance medium was added to each well. Controls included monolayers inoculated with each of the wash/elution agents, and uninoculated cell controls. All plates were incubated in a humidified CO_2 incubator and examined daily.

Recovery of P. aeruginosa from Crushed Waste

The waste used was pre-ground plastic material, including syringes, that had been sterilised by autoclaving. The bacterial culture was P. aeruginosa grown in Nutrient Broth (Gibco) for 24 h at 35°C. The mechanical methods of desorption included blending, shaking, and sonication. For the blending experiments, 5g of crushed waste was added to 45mL of sterile saline in a sterilized blender and blended (liquefy setting) for 2 min. Shaking included placing 5g of waste in a bottle with 45mL of saline and shaking vigorously for 2 min. For sonication, 1g of waste was placed in a sterile test tube and 9mL of saline was added. The material was sonicated for 1 min, vortexed, and then sonicated for another min. Vortexing of the sample was then carried out periodically for 30 min to allow the organisms to recover.

At the beginning of each experiment, a plate count was made of the 24 h culture of P. aeruginosa to determine the CFU/mL. A 300mL volume of Pseudomonas culture was added to a sterile beaker containing 350g of the sterilized waste; the bacteria and waste were then thoroughly mixed. Grab samples were taken as follows: A, C, F and H from the top of the waste in the beaker; and B, D, G and I from the bottom of the beaker. An attempt was made to recover the Pseudomonas organisms from the liquid material and the solid waste before and after processing in the Bio-Murbel machine. The desorption methods used on the samples were as follows: solid sample A was blended; solid sample B was shaken; and solid sample C and D were sonicated. The aforementioned solid samples and sample E, collected from the liquid portion of the waste/culture mix, were taken before the bacteria and crushed waste were processed. For processing, buffered peptone water (APHA) with a pH of 7.2 was used in place of a disinfectant in the Bio-Murbel machine. The machine was allowed to run for 1 min before putting the waste/culture mix through. During processing, the waste was collected in a sterile 4L beaker. Following the crushing treatment, solid sample F was blended, solid sample G was shaken, and solid samples H and I were sonicated. The J sample was taken from the liquid portion of the waste/culture mix. All samples were appropriately diluted in saline and spread plated onto Nutrient Agar (Gibco). The plates were incubated at 35°C for 24 h and the CFU/mL determined. This experiment was repeated three times.

Comparison of Bacterial Desorption Methods

The same procedure was followed as described for the crushed waste recovery study. The bacteria included Serratia marcescens, Staphylococcus epidermidis, grown in Tryptic Soy Broth (Gibco), and P. aeruginosa, cultured in Nutrient Broth (Gibco). Incubation was at 35°C for 24 h. The CFU/mL was determined for each organism and the bacteria were mixed with crushed waste as outlined previously. The waste/culture mix was processed in the Bio-Murbel system using buffered peptone water instead of a disinfectant. After processing, blending and shaking were used to desorb S. marcescens from the crush. P. aeruginosa and S. epidermidis in the crushed waste were subjected to blending, shaking, and sonication. Enumeration of the desorbed organisms was carried out using Tryptic Soy Agar for S. marcescens and S. epidermidis and Nutrient Agar for P. aeruginosa.

Effect of Chlorine and Virkon on Waste Containing P. aeruginosa

The method described for the recovery of P. aeruginosa from crushed waste was followed with the samples being analyzed before and after crushing. A 5.0L volume of either 0.2% Cl or 2% Virkon was added to the Bio-Murbel machine as a disinfectant in place of buffered peptone water.

Sterile saline served as diluent for the Virkon experiments whereas chlorine demand free buffer served as a diluent for the chlorine tests. Each disinfectant was assessed in two separate experiments.

RESULTS AND DISCUSSION

Factors Affecting Chlorine Disinfection

The S. marcescens bacteria were completely inactivated by 10mg/L free chlorine after 30 min at a pH of 4 or 5. With a pH of 9, however, 100 mg/L was needed to produce 100% inactivation within the same period.

P. aeruginosa proved to be more sensitive to chlorine than S. marcescens. For example, 1mg/L free chlorine produced 100% inhibition of the organism within 30 min at pH 5.

Mycobacteria also were inhibited by chlorine more readily under acidic conditions. A 30 min exposure to 10 mg/L free chlorine completely inhibited both M. phlei and M. smegmatis at pH4 whereas at pH10, 100mg/L free chlorine was needed.

Young vegetative cells of B. subtilis and B. megaterium that had not yet produced spores were inactivated by 100mg/L chlorine. However, when B. subtilis cultures were heat treated to eliminate the vegetative cells and leave only spores, it was found that 10,000mg/L free chlorine was not sufficient to produce 100% inactivation within 2 h at pH5.

Elution of Viruses from Crushed Waste

When the zero time and 90 min virus samples were titrated only a very slight difference in titre was noted.

The results of the wash/elution method showed that the eluting agents Tryptose Phosphate Broth, Beef extract and non-fat dry milk in glycine were slightly more efficient than the HBSS. However, even after 10 washes with the eluting agents the virus could still be recovered from the crush itself.

The co-cultivation technique proved to be a more effective method of eluting virus from crushed waste. The tissue culture tubes were examined daily and on day one a good monolayer of cells was observed. After four days, a typical enterovirus cytopathic effect could be seen in all samples.

Tables giving details of the aforementioned data are available upon request.

Recovery of P. Aeruginosa from Crushed Waste

The results showed that, as long as the crushed waste and bacterial cultures were well mixed, the differences in bacterial recovery from different collection sites in the waste were minimal.

As may be seen in Fig. 1, more organisms were recovered from the liquid portion of the mixture, both before and after processing, than from the crush itself. Blending of the crush appeared to produce a slightly higher recovery of *P. aeruginosa* organisms than shaking and sonication. Similar results were produced from all three trials.

Comparison of Bacterial Desorption Methods

Fig. 2 shows the comparative results of the three desorption procedures. Statistical analysis of the data indicated that only the tests using *S. marcescens* yielded a significant difference between blending and shaking techniques.

Previous studies on bacterial adsorption to sediment (Seyfried and Owen, 1979) indicated that if weighed amounts of sediment were added directly to MPN tubes containing appropriate recovery media, the adsorption effect was decreased. Further experiments are planned to study bacterial recovery from crushed waste using the MPN method.

Effect of Chlorine and Virkon on Waste Containing *P. aeruginosa*

P. aeruginosa, mixed with crushed waste, was treated in the Bio-Hurbel machine with 0.2% chlorine or 2% Virkon. Both disinfectants produced 100% inhibition of *P. aeruginosa*, as shown in Figs. 3 and 4. The results from duplicate experiments were similar.

P. aeruginosa, an opportunistic pathogen, is the causative agent of nosocomial infections. It was incorporated in this study because it is an important organism in a hospital setting. However, it should be noted that *P. aeruginosa* is relatively chlorine sensitive in comparison with mycobacteria. Future studies are planned to determine the effectiveness of chlorine and Virkon on other bacteria, phage and viruses in crushed waste.

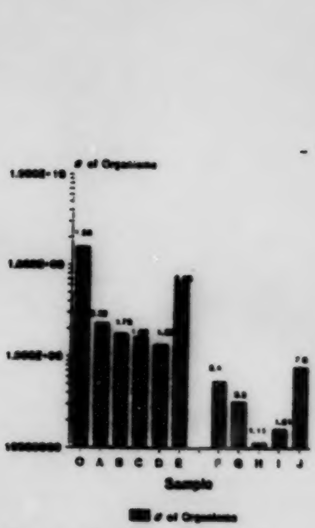

Fig. 1 Comparative recovery of P. aeruginosa from crushed waste.

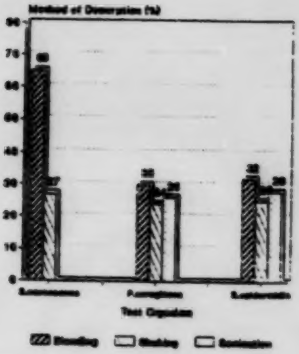

Fig. 2 Bacterial desorption from crushed waste by blending, shaking, and sonication.

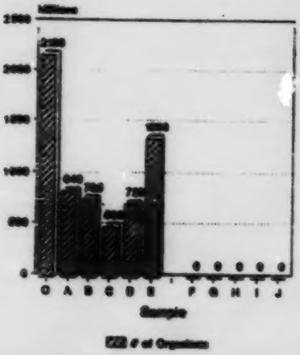

Fig. 3 Effect of chlorine on P. aeruginosa in crushed waste.

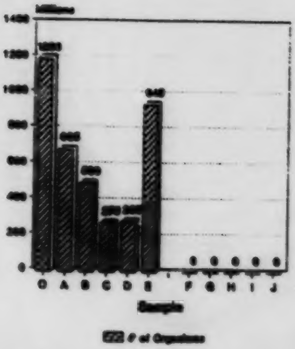

Fig. 4 Effect of Virkon on P. aeruginosa in crushed waste.

LEGEND Sample O = pure culture; samples A to E = before processing;
Samples F to J = after processing; A and F = blended;
B and C = shaken; C, D, H and I = sonicated;
F and J = liquid.

SUMMARY

The effect of chlorine on a pure bacterial culture was tested and it was found that *P. aeruginosa* was the most sensitive to free chlorine; the spores of *B. subtilis* were the most resistant. Different species of the same genus demonstrated similar susceptibilities to chlorine. Lowering the pH and increasing the chlorine concentration and exposure time improved the inhibitory action of chlorine.

The co-cultivation technique was shown to be better than the wash/elution method for the recovery of virus from crushed waste.

Blending, shaking and sonication were used to facilitate the recovery of *S. marcescens*, *P. aeruginosa*, and *S. epidermidis* from crushed waste that had been processed in the Bio-Hurbel machine with buffered peptone water in place of a disinfectant. It was shown that, both before and after processing, a higher level of organisms could be recovered from the liquid than from the crush.

One hundred percent inactivation of *P. aeruginosa* was achieved when the organism was mixed with crushed waste and treated with either 0.2% chlorine or 2% Virkon in the Bio-Hurbel machine.

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VOLUME II

SESSION C

LIQUID & SOLID WASTE RESEARCH

POSTER PRESENTATIONS

CP1

PURIFICATION AND DETOXIFICATION OF TEXTILE DYEBATH EFFLUENT BY ELECTROCHEMICAL TREATMENT

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INTRODUCTION

Wastewater from the textile industry is detrimental to our environment. Although variable in quantity and composition depending upon the production processes and raw materials used, the wastewaters are commonly characterized by a high organic loading and high solids content. Dyebath effluents are, in addition, aesthetic pollutants and may also impede light penetration in a receiving body of water, thus interfering with vital biological processes. Dye effluents also pose the problem of potentially toxic or carcinogenic chemicals entering sewage treatment facilities not specifically designed for them.

RESEARCH OBJECTIVES

1. To evaluate the efficacy of a commercially available electrochemical cell in decolorizing textile dyebath effluent.
2. To evaluate the ability of the electrochemical cell to reduce the acute toxicity of textile dyebath effluent.
3. To determine whether the electrochemically treated dyebath effluent can be recycled in subsequent dyeing operations.
4. To determine the limit, if any, on the number of times treated dyebath effluent can be recycled.

MATERIALS AND METHODS

1. Four specimens of polyester fabric were dyed with each of three of the disperse dyes commonly used in Canada. The dyeings were originally done using only a levelling agent as an assistant; they were then repeated using the following carriers (which are also commonly used in Canada): (1) Carolid RSN, (2) Carolid NOL, and (3) Carolid NN-ISN.
2. All effluents were electrochemically treated by immersion of an electrochemical cell (0.4 amps 5 plates) in 500 ml of effluent for 8 minutes. Precipitation was accelerated by adding a polyacrylamide precipitator. The precipitated sludge was removed by filtration.
3. The acute toxicity of all untreated and electrochemically treated effluents was determined by _Daphnia magna_ bioassay.

4. The treated effluent was used as water in a second dyeing and the dyed samples were evaluated visually for uniformity. The colour was measured using a Hunterlab Color Quest spectrocolorimeter and compared to that of the samples dyed using pure water.

5. Determination of the limit on the number of times treated effluent can be used is now in progress. Effluent from each dye-carrier combination is electrochemically treated and filtered prior to reuse in a subsequent dyeing operation with the same dyes and chemical assistants.

RESULTS

1. Operation of the cell at 0.4 amps for 8 minutes released sufficient iron to permit optimal removal of residual dyestuff from the disperse dye effluent. This amount was determined to be 280 mg/l.

2. The acute toxicities of the three dyes, when used in combination with the three carriers, was reduced in all cases. The average decrease in toxicity of dyebaths containing the carriers Carolid RSN, Carolid NOL and Carolid MN-ISN was 186%, 182% and 107%, respectively. The dye Cibacet Yellow-E 4RLF showed an overall greater decrease in toxicity than either of the other two dyes (table 1).

3. The electrochemically treated, filtered effluent which was used for the final dyeings contained substantial amounts of iron but no dyestuff. The specimens dyed with each of the dye-carrier combinations were level with no dyespots, and would be considered commercially acceptable.

4. In general, replicate specimens dyed using fresh water showed less colour variation than did those dyed with recycled effluent. The greater colour variation in the latter specimens is probably due to the presence of iron in the dyebath.

5. The colour difference between the control samples & those dyed using recycled effluent for all dye-carrier combinations was greater than recommended tolerances (table 2). When the effluent was filtered twice prior to recycling, color differences between samples dyed using fresh and recycled liquor were, in most cases, within commercially acceptable limits.

6. Ongoing research indicates that, when Resolin Blue FBL is applied with each of the three carriers, two (Carolid NOL and Carolid MN-ISN) can be used for at least nine dyeings with commercially acceptable colour differences. All dyeings performed using treated effluent containing Resolin Blue FBL/Carolid RSN are beyond commercially acceptable colour limits.

7. Our data indicate that recycling of electrochemically purified, filtered dyebath effluent can give commercially acceptable results provided that dyes and carriers are properly selected. It is likely that each dyebath formula will have to be pre-tested to determine the optimal purification procedure.

SUMMARY

1. The electrochemical treatment used in this research was highly effective in removing colour from the disperse dye effluents tested.

2. Toxicity of the effluent was substantially reduced by the electrochemical treatment.

3. Reuse of the treated effluent resulted in first quality dyeings although there were colour differences in specimens dyed using the fresh and the recycled liquor. The colour differences were markedly reduced by increasing the number of filtration processes.

4. In some cases, treated effluent can be repeatedly reused without adverse effect on the quality of the dyed fabrics.

IMPLICATIONS

The research suggests that electrochemical treatment of dyebath effluent removes colour so that the effluent can be successfully recycled in subsequent dyeing processes. Alternatively, if the effluent is released into the environment, the treatment significantly reduces its acute toxicity.

TABLE 1

SUMMARY OF ACUTE TOXICITY TO DAPHNIA MAGNA OF DYES BEFORE AND AFTER ELECTROCHEMICAL TREATMENT

Dyestuff	Carrier	LC_{50} Before Treatment	LC_{50} After Treatment	% Decrease in Toxicity
Resolin Blue FBL	Carolid RSN	35.4	70.7	99.7
Resolin Red FRL	Carolid RSN	27.8	35.4	27.3
Cibacet Yellow E 4RLF	Carolid RSN	12.0	63.7	430.8 $\bar{x}$ = 185.9
Resolin Blue FBL	Carolid NOL	13.7	21.8	59.1
Resolin Red FRL	Carolid NOL	10.3	31.8	208.7
Cibacet Yellow E 4RLF	Carolid NOL	16.2	61.4	279.0 $\bar{x}$ = 182.3
Resolin Blue FBL	Carolid MN-ISN	52.6	70.7	34.4
Resolin Red FRL	Carolid MN-ISN	19.9	35.4	77.9
Cibacet Yellow E 4RLF	Carolid MN-ISN	18.0	55.4	207.8 $\bar{x}$ = 106.7

TABLE 2

COLOUR DIFFERENCES BETWEEN SAMPLES DYED USING FRESH AND RECYCLED EFFLUENT

Dyestuff	Carrier	Total Color Difference[*] (ΔE)
Resolin Blue FBL	Carolid RSN	3.03
Resolin Red FRL	Carolid RSN	0.71
Cibacet Yellow E 4RLF	Carolid RSN	2.76
Resolin Blue FBL	Carolid NOL	6.08
Resolin Red FRL	Carolid NOL	1.00
Cibacet Yellow E 4RLF	Carolid NOL	7.66
Resolin Blue FBL	Carolid MN-ISN	1.73
Resolin Red FRL	Carolid MN-ISN	1.15
Cibacet Yellow E 4RLF	Carolid MN-ISN	8.11

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[*] 1.00 is considered the maximum ΔE value for commercial acceptability.

CP2

STABILIZATION OF A WASTE IN A LANDFILL ENVIRONMENT.

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INTRODUCTION

The use of landfill disposal continues to be the most widely used system for disposal of municipal refuse. Despite the long history of landfill use, the impact of the landfill on the surrounding environment and aquifer remains controversial. Although the initial content of the landfill can be estimated with reasonable accuracy, the rate and extent of material transfer to the environment is not well defined. Part of the difficulty is in quantifying the parameters that control the chemical and biological reactions occurring within the landfill mass. Knowledge of these parameters is critical in determining environmental impact and in improving the design of long term landfill sites.

While field studies of existing landfills provide valuable information, there is little opportunity to modify controlling parameters to quantify their significance. On the other hand, laboratory studies generally have not been able to duplicate field behaviour and thus lack applicability for environmental modelling. This study has employed large scale laboratory leaching columns which were designed to simulate landfill behaviour. There are 16 columns in operation packed with 4 different compositions: 100% municipal solid waste(MSW), MSW + 8% industrial waste(IW), MSW + 30% IW and 8% IW in sand. The high density polyethylene cylindrical columns are 1.93m high, and 0.33m in diameter and contain approximately 43 kg (dry weight) of MSW. One half of the columns receive moisture input from precipitation while the other half receive controlled periodic water additions. The systems are maintained in unsaturated flow conditions with regular leachate removal from the bottom reservoirs. As a result of their size the columns are operated in an outside location. This scale of experimentation, though large for laboratory studies, is required for developing the landfill hydrodynamics and biological activity.The role of hazardous waste was studied using a selected hazardous waste at 8 and 30 weight percent of the municipal refuse content. The waste was added in layers in the test cells. The effect of hazardous waste in a landfill site is not well understood. Several studies have indicated little change of leachate quality with a variety of wastes. A serious concern with hazardous wastes is the long term behaviour in the landfill environment which goes through several phases before final stabilization. The effects of the hazardous wastes may not be apparent until the buffering capacity of the landfill is lost. The leachate quality of a variety of test cells has been studied over an extended period (5 years) and the effects of the hazardous waste addition to the test cells are examined.

RESULTS and DISCUSSION

Previous work has demonstrated that the behaviour of the test cells containing municipal refuse is similar to that observed in medium and large field cell studies. The comparison was based on the concentration behaviour of 8 elements (Cu, Zn, Fe, Na, K, Cl, Mn, Mg), COD and pH. Of interest in this phase of the research is the stabilization of the MSW and of the industrial solid waste.

The industrial waste composition is shown in the table. The waste was very fine and highly alkaline. The Regulation 309 leachate test showed lead solubilization to be above the guidelines.

LEAD

The studies of lead solubilization from the waste disposed in sand columns revealed very high concentrations during the initial 6 months. Over the 5 year period, 6% of the total lead has been leached from the test cells containing sand. Though low levels < 1 mg/l are now found in the leachate, the pH is still alkaline (10).

From test cells containing the same mass of industrial waste but having MSW instead of sand and assuming that only the industrial waste contributed to the lead values, only 0.034% of the lead leached over the same period. For the test cells having a 30% industrial waste loading, the total lead leached was the same but the percent leached was only 0.006%. Test cells having only MSW and no industrial waste have leached twice the amount of lead found from cells with industrial waste. The beneficial effect produced by the industrial waste appears to be related to the alkalinity of the waste.

CADMIUM

The cadmium levels in the industrial waste were low (0.04%). For this element the level of alkalinity in the leachate served to suppress cadmium mobility. The sand columns, with pH=10, leached only $7x10^{-4}$% of the total cadmium in the waste. The MSW columns with 30% industrial waste loading, leached $6x10^{-2}$%, while the MSW columns with the same mass of industrial waste leached 1.2% of the total cadmium. The MSW columns with no industrial waste had the highest cadmium release rate with 1.3x the level of the MSW columns with 8% industrial waste. An interesting feature of the cadmium release from the MSW columns with industrial waste is that the rate of release has been increasing during the past year. This is at a time when BOD and pH have been stable.

ZINC

The industrial waste contains substantial levels of zinc (14%). The alkalinity of the leachate of the waste from the sand column resulted in only $4.3 x10^{-3}$% of the zinc from leaching from the column during the 5 year period. Interpreting the contribution to zinc leached from the MSW with the same mass of industrial waste is complicated by the high level of zinc from the MSW alone. The average amount of zinc leached from each MSW column was 3.63g per column. The mass leached from the industrial waste in sand was 0.019g per column. The same mass of industrial waste in MSW resulted in 0.47g of zinc being leached. Higher levels were found from columns with

30% industrial waste loading (1.92g) though still not at level found in the MSW columns.

OTHER ELEMENTS (Cu, Mn, Ca, Cr, Fe, Co)

The concentration of these elements in the industrial waste are shown in the Table. The addition of the industrial waste to MSW did not increase the concentration of the element in the leachate. The release of these elements from columns with the MSW was equal to or greater than from the columns with the additional 8% industrial waste. The columns having the alkaline solid waste generally showed much cleaner leachate (lower COD) and lower percentage of metals released. The low levels of metals released from the sand columns is a consequence of the low solubility of these elements in the alkaline leachate.

There is a good evidence that MSW has the capacity to inhibit the release of some metal values from wastes. This capacity is very beneficial in reducing the impact of the waste on the environment. This absorption capacity has been reported for a number of codisposal tests but the mechanism of metal retention suggested (either adsorption or precipitation) has not been proven. A more interesting possibility shown by the current research is that the presence of an alkaline waste can have a significant influence on the MSW leachate behaviour. The evidence from the study indicates that there is a reduced biological activity in the columns with industrial waste and this is supported by smaller values of total COD from the codisposal columns. Despite the low level of biological activity and low values of metals leaching from the columns, there is no direct evidence that the wastes have been stabilized. Most of the metal values remain in the MSW and have not been leached. The remobilization of cadmium after two years of low activity has not been explained.

In the next phase of the research we have proposed to investigate the chemical changes induced in the industrial waste in the MSW environment and to determine the extent of metal ion mobility in the MSW.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the Ontario Ministry of the Environment and the technical support and encouragement provided by Mr. M.B. Fielding and Dr. J. Pimenta of the Ontario Ministry of the Environment.

TABLE

ANALYSIS OF THE INDUSTRIAL SOLID WASTE[1]

Element	Fe	Zn	Ca	Mn	Pb	Cr	Cu	Cd
Total Mass(g)	851	441	388	128	61.7	6.57	5.63	1.02
Weight Percent	27.2	14.1	12.4	4.1	2.0	0.21	0.18	0.030
Leachate Analysis for Industrial Waste in Sand								
Mass Leached(g)	0.023	0.019	69.2	1.46	3.53	0.068	0.0135	0.0007
% Leached	2.7×10^{-3}	4.3×10^{-4}	17.8	1.1	5.7	1.0	0.24	7×10^{-4}
Leachate Analysis for Industrial Waste in MSW								
Mass Leached(g)	17.2	0.468	72.5	0.79	0.021	0.013	0.016	0.0126
% Leached	2.02	0.106	18.7	0.62	0.034	0.20	2.8	1.2
Leachate Analysis for MSW								
Mass Leached(g)	104.7	3.63	378.9	3.41	0.049	0.16	0.050	0.0169

The mass of industrial waste used in each column was 3.13 kg. The values reported in the table are the averages from 4 test cells for each condition (MSW, MSW+8% industrial waste, sand + industrial waste).

[1] The principal chemical species are in simple and complex oxide forms which include iron spinels and silicates.

VOLUME II

SESSION D

ANALYTICAL METHODS RESEARCH

VERBAL PRESENTATIONS

D2

COUPLING AN EXTERNAL SOURCE TO A FOURIER TRANSFORM ION CYCLOTRON RESONANCE SPECTROMETER TO IMPROVE ITS USE FOR ANALYTICAL PURPOSES.

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These days magnetic sector and quadrupole mass spectrometers are of prime importance for analysis in environmental research. To date the Fourier transform ion cyclotron resonance (ICR) spectrometer has not been considered seriously in analytical laboratories. This can partly be ascribed to the ultra high vacuum necessary for analysis, rendering chemical ionization, fast atom bombardment and coupling with a gas chromatograph impossible.

To extend the analytical capability of our Spectrospin CMS 47 Fourier transform ion cyclotron resonance spectrometer, we have successfully mated it with an external ionization source. In the external source sample material can be ionized via fast atom bombardment and chemical ionization. (Coupling with a gas chromatograph is possible as well, but it has not yet been installed.) Differential pumping ensures that the ICR cell is still at very low pressure ($< 5 \times 10^{9}$ mbar). This instrument is thus ideally suited for the analysis of a wide variety of materials and offers the advantage over magnetic sector and quadrupole mass spectrometers that (i) the ionized material can be detected with superior mass resolution ($m/\Delta m > 1 \times 10^{6}$ at m/z 115) and (ii) MS^{n} experiments are possible without hardware changes. In addition, ion-molecule reactions of the ions externally generated can be studied in the ICR cell, which will lead to a better understanding of the processes taking place in chemical ionization.

We have used this technique to study a wide variety of organic pollutants, in particular phenols and polyhalogenated compounds. Chemical ionization is the preferred route for ionization. Collision induced dissociation and ion-molecule reactions of these ions leads to a better understanding of the chemical ionization process. Higher mass bio-organic and organometallic can successfully be analyzed with fast atom bombardment. Admission of ambient air to the high pressure source allows analysis of air containing volatile pollutants as well.

Thus, a Fourier transform ion cyclotron resonance mass spectrometer with an external source combines high pressure ionization techniques (for involatile, higher mass sample material) with high mass resolution detection.

D3

THE ANALYSIS OF N-NITROSODIMETHYLAMINE IN ENVIRONMENTAL SAMPLES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY.

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INTRODUCTION

N-nitrosodimethylamine (NDMA) is a potent carcinogen found in tobacco smoke, food and beverages, industrial processes, water treatment processes and in the biosphere. The identification of NDMA in drinking water samples resulted in the need for an accurate determination of NDMA in various aqueous samples at the low part per trillion (ppt) level. NDMA is very soluble in water and is therefore difficult to extract. Also, its polarity makes it difficult to chromatograph on standard non-polar phase columns. The presence of chemical interferences causes difficulties in the identification and quantitation of NDMA because of the common low mass ions that are monitored. These difficulties require that a method for NDMA be selective and sensitive. The advantages and disadvantages of the various GC/MS techniques are discussed.

EXPERIMENTAL SECTION

Extraction Procedure:

Particulates in the sample were removed by filtering the sample through pre-extracted glass wool. The internal standard, d_6-NDMA, was added to the sample and the sample mixed thoroughly. The pH of the sample was adjusted to 10-12 by addition of a sodium hydroxide solution. The sample was serially extracted three times with dichloromethane. The combined dichloromethane extract was washed with a dilute sulphuric acid (pH 2) solution and then filtered through anhydrous sodium sulphate. The extract was concentrated to 200 uL.

Low Resolution Mass Spectrometry (LRMS):

Full scan GC/MS work was done on a Finnigan 4500. The mass range scanned was m/z 35-510 in 0.80 seconds. GC analysis was performed on a DB-5 (60m x 0.32mm i.d.) column.

Selected ion monitoring (SIM) studies were performed on an HP-5970 MSD. The ions monitored for NDMA were m/z 74 and m/z 42 with dwell times of 150 ms and 50 ms, respectively. Ions monitored for d_6-NDMA were m/z 80 and m/z 46, with dwell times of 150 ms and 50 ms, respectively. A DB-1701 (30m x 0.25mm i.d.) column was used for the GC analysis. Additional SIM work was performed on the VG ZAB-2F at 1000 Resolving Power (RP).

High Resolution Mass Spectrometry (HRMS):

The VG ZAB-2F, a double focusing reverse geometry magnetic sector mass spectrometer, was tuned to 7000 RP for the high resolution work. A lockmass (m/z 68.9952, PFTBA) and the exact masses of NDMA (m/z 74.0480) and d_6-NDMA (m/z 80.0857) were monitored. Dwell times were 100 ms for m/z 74.0480 and 50 ms for m/z 68.9952 and m/z 80.0857.

Quantitation of NDMA was accomplished by standard isotope dilution.

RESULTS AND DISCUSSION

NDMA does not chromatograph well on a DB-5 column. Alternate phases that gave better chromatography and sensitivity were DB-17 and DB-1701. However, there were still problems with co-elution of interferences.

A single quadrupole mass spectrometer in the full scan mode does not have the sensitivity to detect low ppt levels of NDMA in drinking water. However, it offers a degree of selectivity because interferences can be monitored in the mass spectrum. The instrument detection limit was 10 ng injected on a DB-5 column routinely used for characterization of extractable organics. The method detection limit for full scan GC/MS was 2 ug/L.

The mass spectrum of NDMA consists of a molecular (quantitation) ion at m/z 74 (base peak) and an intense fragment (qualifying) ion at m/z 42 . In the SIM mode, using a single quadrupole mass spectrometer, sensitivity has been increased over full scan MS but some selectivity is lost due to the presence of co-eluting interferents with the same nominal masses, m/z 42, 74, 46 and 80. This limits the usefulness of a single quadrupole mass spectrometer for the determination of NDMA, as co-eluting interferences could give erroneous results. The instrument detection limit was 20 pg injected. The method detection limit was 25-50 ng/L. The linear dynamic range was from 20 pg to 15 ng.

The VG ZAB-2F at low resolution (1000 RP) in the SIM mode is more sensitive than a quadrupole mass spectrometer in SIM mode for the quantitation ion (m/z 74) (200 fg injected). However, due to the voltage switching technique m/z 42 is weak relative to m/z 74.

In order to detect low ppt levels of NDMA confidently, the effects of chemical interferences co-eluting with the NDMA must be eliminated. Methyl esters are a common compound class that give rise to ions at m/z 74. To differentiate them from the NDMA, the VG ZAB-2F was run > 7000 RP. NDMA samples run at > 7000 RP in the single ion monitoring mode had excellent sensitivity and selectivity. This permitted the low ppt detection of NDMA with an instrument detection limit of < 1 pg. Procedure blanks showed a 1-4 ng/L level of NDMA and therefore the method has a detection limit set at 5-10 ng/L. The linear dynamic range for these parameters was 2 pg to 40 ng.

CONCLUSION

Of the techniques evaluated, single ion monitoring at > 7000 resolution is the method of choice because of its superior sensitivity, selectivity and linear dynamic range. This allows the determination of NDMA in environmental samples to be at the low ppt level.

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D4

REAL TIME MEASUREMENTS OF DIMETHYLNITROSAMINE IN AMBIENT AIR BY MOBILE TANDEM MASS SPECTROMETRY

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ABSTRACT

Analysis of trace quantities of air toxics is becoming increasingly important in air pollution research. Dimethylnitrosamine (DMNA), O=N-N-$(CH_3)_2$, is a potent carcinogen reportedly found in tobacco smoke, cured meats and in some industrial processes involving the interaction of nitrite and dimethylamine. The real time detection of ppt levels of DMNA requires reliable sampling and calibration techniques, as well as, sophisticated analytical instrumentation. A method for DMNA detection was developed for mobile air monitoring applications using an atmospheric pressure chemical ionization (APCI) triple quadrupole (Q1, Q2, Q3) mass spectrometer (TAGA 6000). To calibrate the TAGA, a heated nebulizer was developed for injecting aqueous standards directly into the air sampling inlet of the analyzer. The nebulizer which consists of a capillary tube for liquid sample injections and two outer concentric stainless steel tubes for purge and carrier gases provides for the addition of controlled amounts of DMNA into the ion source. The ion chemistry of DMNA under ammonia APCI conditions is relatively simple: DMNA molecules undergo proton transfer reactions with ammonium ions (NH_4^+) to yield parent ions at 75 amu (atomic mass units). Parent ions, selected in the first quadrupole (Q1), undergo collisional activated dissociation (CAD) with argon in Q2 (RF only). The resultant daughter ions at 15, 43 and 58 amu are identified by Q3. Multiple reaction monitoring (MRM) of the parent/daughter ion pairs 75/15, 75/43 and 75/58 is used to monitor DMNA in real time. The response of the TAGA system to DMNA was characterized through six-point calibration curves, in the concentration range of 0 to 80 ng/m^3. Low detection limits and reproducible calibration data were accomplished by the optimization of various MS/MS and nebulizer parameters. This unique method was recently applied to an air monitoring study in Ontario where DMNA was measured and tracked to its source using the mobile TAGA 6000. The real time limits of detection for DMNA were better than 5 ng/m^3 (2 ppt) during a two-week field survey.

INTRODUCTION

Real time detection and quantification of air contaminants at trace levels require sensitive instrumentation and advanced calibration techniques. Recently there was a need for the development of a method to detect dimethylnitrosamine (DMNA), O=N-N-$(CH_3)_2$, with high specificity supported by accurate calibrations. In 1989, a preliminary study conducted using the Ministry's TAGA 3000, a single quadrupole mass spectrometer (MS), showed that DMNA can be detected at levels as low as 15 ng/m^3 in real time. Depending on the ionization technique and the complexity of the sample matrix, identification of contaminants with single MS systems may be tentative. Thus, detailed research on DMNA method of detection was performed with the Ministry's mobile TAGA 6000 triple quadrupole mass spectrometer. Owing to the superior analytical capabilities of tandem mass spectrometry, difficulties of contaminant identification are greatly reduced while maintaining real time detection. The mobile TAGA 6000 has been used for on-site analysis of numerous contaminants from a variety of industrial sources in Ontario, and during environmental emergencies such as the Hagersville tire fire in February 1990. The successful application of the TAGA 6000 depends primarily on well established quality assessment/quality control (QA/QC) programs and optimum instrumentation performance. For this study it was necessary to develop and evaluate the performance of a heated nebulizer for injecting controlled amounts of DMNA liquid standards into the TAGA ion source. The standard injection technique was used for calibration purposes and for establishing the real time limits of detection for DMNA. This novel method was recently applied to an air monitoring survey in which trace levels of DMNA were measured.

EXPERIMENTAL

A schematic diagram of the TAGA 6000 is shown in Figure 1. The basic operation is governed by the principles of tandem APCI mass spectrometry. Parent ions, formed in the APCI region, pass through an orifice into the vacuum chamber where they are separated by the first quadrupole and fragmented with argon gas in the second quadrupole (RF only). The resultant fragments, or daughter ions, are analyzed by the third quadrupole. Compound identification is achieved by comparison of the daughter ion spectra to a standard CAD (collisionally activated dissociation) library spectra. Compound quantification is accomplished by calibrating the response of the TAGA to known amounts of the calibrant admitted into the inlet air flow.

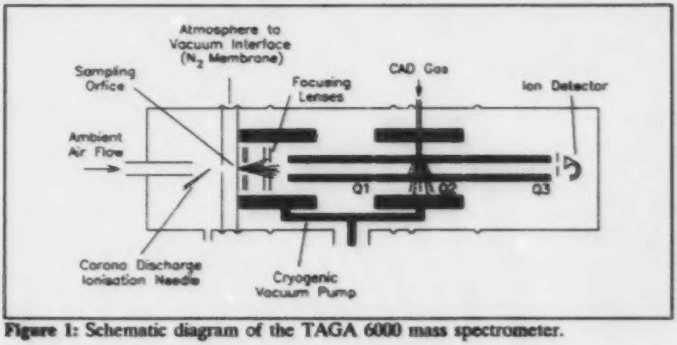

Figure 1: Schematic diagram of the TAGA 6000 mass spectrometer.

Optimization of ion signals and calibration of the TAGA sensitivity were achieved by introducing known amounts of DMNA-water solution into the ion source. DMNA photo-degrades upon exposure to sunlight; consequently, DMNA standards were wrapped in aluminum foil and stored in a cool, dark area. Calibrations were performed under minimum exposure to light.

The DMNA aqueous standard (8.04 ng/L) was introduced into the inlet air flow via a heated nebulizer developed by the Mobile Monitoring Group. A schematic diagram of the nebulizer is shown in Figure 2. The nebulizer consists of a capillary tube for liquid sample injections and two outer concentric stainless steel tubes for nebulizing and purging gases; this configuration ensures uniform sample atomization thus providing for the addition of controlled amounts of DMNA into the TAGA ion source. The calibrant was injected into the nebulizer with a 0.5 mL, 22s gauge Hamilton Gastight syringe mounted in a Harvard (model 22) syringe infusion pump. The flow rates of DMNA into the TAGA ion source were controlled by the speed of the pump. Flow rates 0 to 0.9 μL/min allowed a DMNA concentration range of 0 to 80 ng/m^3 to be generated in the APCI source. Higher flow rates were also used to examine the linearity of the response curves at concentrations up to 4000 ng/m^3.

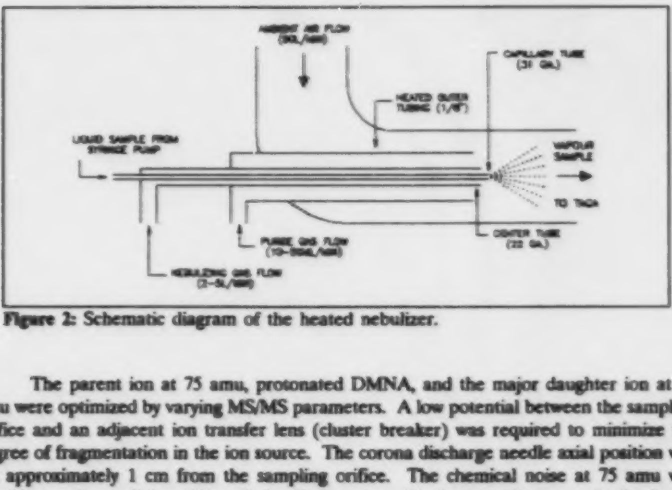

Figure 2: Schematic diagram of the heated nebulizer.

The parent ion at 75 amu, protonated DMNA, and the major daughter ion at 43 amu were optimized by varying MS/MS parameters. A low potential between the sampling orifice and an adjacent ion transfer lens (cluster breaker) was required to minimize the degree of fragmentation in the ion source. The corona discharge needle axial position was set approximately 1 cm from the sampling orifice. The chemical noise at 75 amu was sensitive to the radial position of the discharge needle; best results were obtained with the tip of the discharge needle slightly off center (ca. 0.5 mm) with respect to the sampling orifice.

The temperature of the inlet air was maintained at 50 °C in order to maximize ion signals and minimize memory effects. Several temperature settings were used for the nebulizer; in terms of DMNA signal stability, satisfactory results were obtained by operating the nebulizer in the range of 30 to 50 °C.

RESULTS AND DISCUSSION

The response of the TAGA to DMNA and the chemical background were examined under water and ammonia CI conditions. Owing to the higher proton affinity of NH_3 as compared to that of H_2O, ammonia CI simplifies the mass spectra of complex air samples. Ammonia CI suppressed the background (viz. chemical noise) by at least a factor of 10 over H_2O CI, allowing for lower detection limits. The chemical noise under ammonia CI conditions was only 1 to 2 ion counts per second (ICPS) for the three parent/daughter ions of DMNA.

The ion chemistry of DMNA gas under TAGA/APCI conditions is relatively simple: DMNA molecules undergo proton transfer reactions with hydronium ions (H_3O^+) or ammonium ions (NH_4^+) to yield parent ions at 75 amu (atomic mass units). Fragmentation of protonated DMNA in the APCI source was found to be negligible. Under collisionally activated dissociation (CAD) daughter ions at 43, 15 and 58 amu were observed. The possibility of DMNA produced in the ion source from dimethylamine (DMA) and oxides of nitrogen was ruled out; when 200 ppb of DMA and 1% NO was admitted into the TAGA source, DMNA was not observed.

An MS/MS library ion mass spectrum for DMNA was created using 50 eV ion energy and argon CAD gas thickness of 300 x 10^{12} molecules/cm^2. The CAD fragmentation pattern, shown in Figure 3 (bottom), is dominated by three daughter ions at 15, 43 and 58 amu. Figure 3 (top) shows daughter ion spectra for m/z=75 amu obtained downwind of a chemical plant. The CAD spectra of the "unknown" is compared

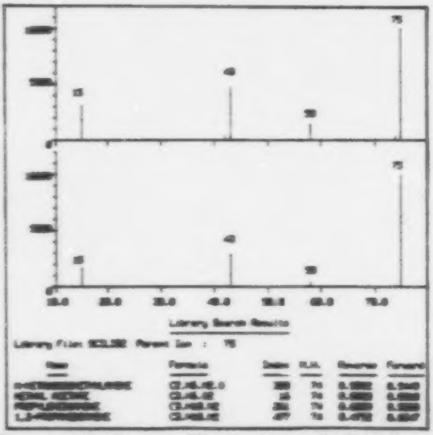

Figure 3: The CAD spectra for the mass 75 parent ions obtained downwind of a chemical plant (top) and CAD library mass spectrum of DMNA (bottom).

with standard CAD library spectra; agreement between the "reverse" and "forward" library search results and their closeness to unity, indicate the degree of certainty for compound identification. The "best" search results were obtained for DMNA. A closer examination of the CAD spectra of the second listing showed that methyl acetate lacks the 58 amu fragment.

Six-point calibrations of DMNA were performed by simultaneously recording the responses of three parent/daughter (P/D) ion pairs. An example of a calibration, in the concentration range 0 to 80 ng/m^3 is shown in Figure 4; these data were obtained under ammonia CI conditions. The slopes of the response curves are measures of the sensitivity of the APCI MS/MS system to DMNA. To avoid system contamination, the saturation point for response non-linearity was not determined; however, linear response was observed up to 4000 ng/m^3 DMNA.

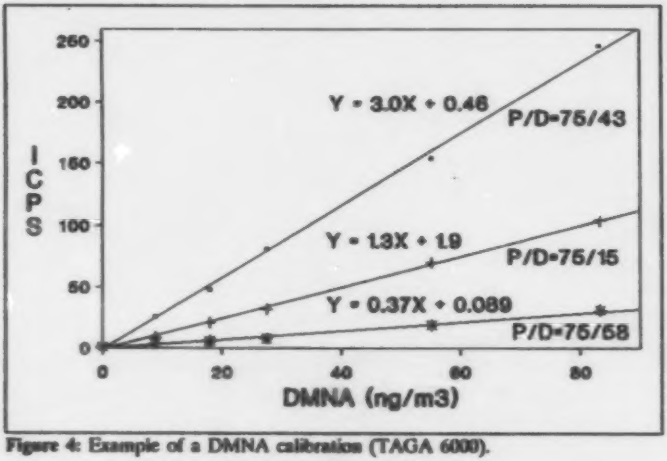

Figure 4: Example of a DMNA calibration (TAGA 6000).

Figure 5 shows the detection limits (DL) for DMNA, based on the average of the DL values of the three parent/daughter ions. Detection limits are defined as 3 times the standard deviation of the background signals divided by the sensitivity, or the slope of the response curve. Detection limits in ambient air were determined at various locations in selected cities in southern Ontario over a period of several days. The variation in DL values from day to day is readily apparent: the DL's ranged from 2.9 to 4.8 ng/m^3 with a mean value of 3.8 ng/m^3 and a standard deviation of 0.67 ng/m^3.

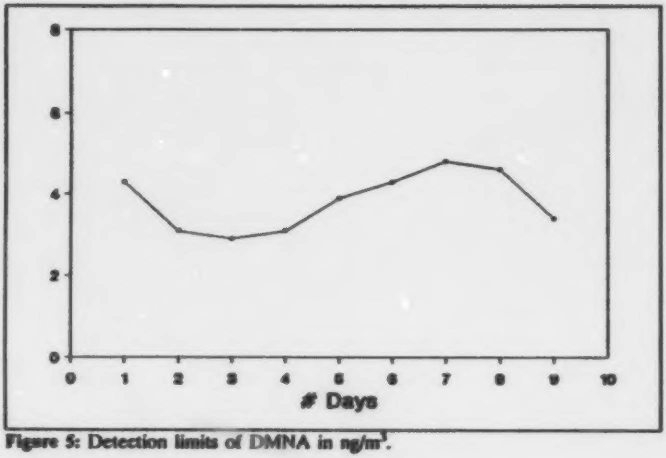

Figure 5: Detection limits of DMNA in ng/m^3.

The detection limits are affected most by the ambient air matrix, the measurement dwell time and the position of the corona discharge needle relative to the sampling orifice. For instance, slight changes in the radial position of the discharge needle can alter signal stability and, subsequently change detection limits. Also, longer measurement dwell times produce lower detection limits; for example, a dwell time of 1 second results in a detection limit of 3 ng/m^3 whereas a dwell time of 0.1 seconds yields a DL of 30 ng/m^3.

This method was field-tested in the spring of 1990 by conducting an air monitoring survey of DMNA in the vicinity of a suspected source. During the two-week survey, DMNA detection limits were determined at least twice daily; on average, the DLs were better than 5 ng/m^3. Ambient DMNA levels were recorded at several locations both upwind and downwind of the source. Figure 6 (a) shows the real time measurements of DMNA recorded every 5 seconds for a period of 30 minutes at a fixed location downwind of the source. Rapid changes in DMNA levels were mainly due to variations in the wind direction. The downwind response profiles of the parent/daughter ion pairs are similar indicating the presence of DMNA. In contrast, data obtained upwind, Figure 6 (b), show that changes the parent/daughter ion profiles do not correlate, indicating the absence of DMNA.

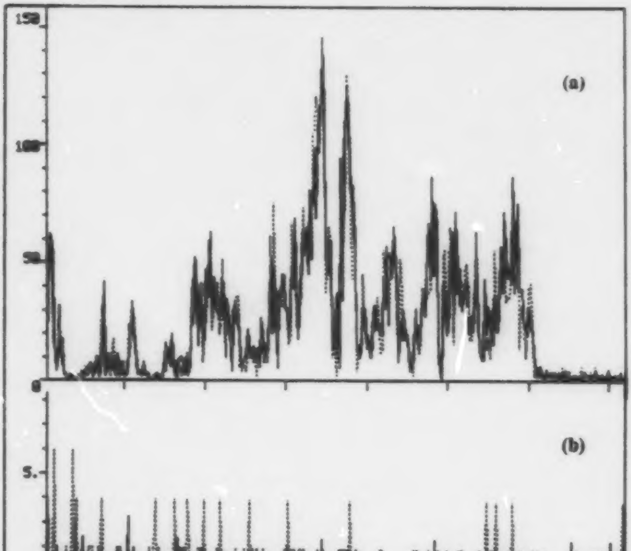

Figure 6: Real time monitoring of DMNA downwind of a chemical plant (a) and background levels of ion pairs 75/15, 75/43 (b). Y-axis are in ng/m^3.

Dimethylnitrosamine was also measured while the mobile TAGA criss-crossed the streets downwind of the plant. Figure 7a shows an example of plume tracking data; the concentration of DMNA varied with distance from the source: 51 ng/m^3 were recorded at 300 m and 21 ng/m^3 at 600 m. At distances greater than 1 km, DMNA was not detected. Figure 7b shows the real time data as recorded by the TAGA while transecting the plume at various distances from the source.

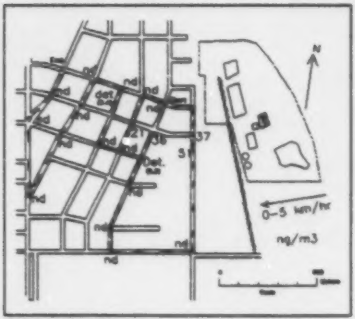

Figure 7a: Plume tracking for DMNA downwind of a chemical plant.

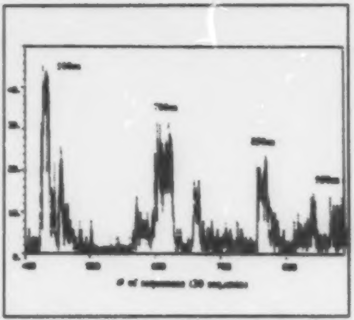

Figure 7b: Plume tracking concentration profile of DMNA in ng/m^3.

SUMMARY

The Mobile Monitoring Group of the Air Resources Branch developed a new method to monitor, in real time, trace amounts of atmospheric DMNA based on the Ministry's mobile TAGA 6000, an APCI/MS/MS system. Several results were obtained from this study. Ammonia is the preferred CI reagent for monitoring DMNA in ambient air, since it reduces the number of interferences through selective ionization. Compared with water CI, ammonia CI gave considerably lower background levels, improving specificity and lowering detection limits. A calibration procedure for injecting aqueous DMNA standards through a heated nebulizer which was developed, proved to be reliable and reproducible at final gas phase concentrations up to 80 ng/m^3. The *real time* limits of detection of DMNA in ambient air was of the order of 5 ng/m^3 or 2 ppt. This unique technique was applied to measuring ambient DMNA levels in Ontario.

D6 *CANVIRO Analytical Laboratories Ltd.*

THE ANALYSIS OF SMITHVILLE DRINKING WATER FOR PCBs

D.A.Sutherland * , J.Waugh, L.Paul, A.Rayner, G.Reuel

The remediation of a waste storage site contaminated with polychlorinated biphenyls (PCBs) near Smithville Ontario is a high priority and high profile project. The importance of protecting public drinking waters and the inherent high costs of remediation underscore the need for comprehensive QA/QC, confidence in the analytical result and a turnaround time for analytical results that allows for responsive action. After considerable Research and Development funded by CANVIRO Laboratories, and method performance testing by the Ministry of the Environment (MOE), CANVIRO Laboratories was awarded a multi-year contract to analyze groundwater for PCBs and report these results immediately to the Ministry.

Traditionally the detection of PCB's has relied on the electron capture detector (ECD). Any contentious samples identified using this technique were often sent to a mass spectrometry department in hopes that a confirmatory analysis could be made. Often the sensitivity of the GC/MS was insufficient.

To reduce the time and costs in obtaining results for this project, CANVIRO Laboratories developed a method to analyze PCB's in waters at the required low limits of detection directly by GC/MS on a routine basis, thus providing simultaneous low level detection and positive confirmation.

MOE DETECTION REQUIREMENTS vs CANVIRO PERFORMANCE (ppb)

	MOE "w"	CANVIRO "w"
1,2,4-TCB	0.005	0.002
1,2,3-TCB	0.005	0.002
Arochlor 1242	0.020	0.005
Arochlor 1254	0.020	0.010
Arochlor 1260	0.020	0.010

TCB - Trichlorobenzene
w - range 0.5-1.0 standard deviations from low level replicate analyses

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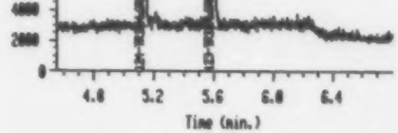
The analysis by GC/MS is relatively free from the influence of co-eluting pesticides and phthalates that can and do interfere when using an ECD detector. The absence of any clean-up steps in CANVIRO's procedure and the reasonable concentration factors (ie., 800 mL sample to a final 1 mL extract) provide excellent method precision. The operating conditions of the GC/MS and typical demonstrations of method sensitivity are presented below.

Instrumental Parameters:

HP - MSD System:
5890 - Gas Chromatograph
5970B - Mass Selective Detector
7673A - Robotic Autosampler
Carrier Gas : Helium
Temp Program : 90°C for 0.4 min,
Ramped @15°C/min to 130°C
Ramped @ 5°C/min to 270°C
Ramped @20°C/min to 315°C
Final Hold 1 min
Injector Temp : 280°C
Interface Temp: 290°C
Splitless Time: 0.4 min
Column: RTX-5, 60 metre x 0.25 mm ID
x 0.25 phase thickness

Demonstrated Sensitivity

6 Picograms Injected of
1,2,4 and 1,2,3-Trichlorobenzenes



Sample Extractions:

A liquid-liquid extraction is carried out using a magnetic stir plate and teflon stir bar. Each 800 mL sample is extracted with 60 mL of methylene chloride, in the original sample bottle after the addition of a teflon stir bar. After 20 minutes of vigourous mixing, a separatory funnel is used to separate the solvent and aqueous phases. The aqueous phase is extracted in the sample bottle with two more 60 mL methylene chloride aliquots.

The extracts are dried with anhydrous sodium sulphate and concentrated to a volume of 1 mL via rotary evaporation. No clean-up or fractionation methods are required due mostly to the specificity of GC/MS.

Identification and Quantification:

The GC/MS in the Selected Ion Monitoring (SIM) mode is very specific. Selected ion groupings effectively make the GC/MS into a cogener specific detector.

Many excellent publications have shown identification strategies that include multiple regression, least squares analysis or pattern recognition software. CANVIRO Laboratories modified MOE's Webb and McCall method and have developed the following rules that are more easily integrated into a routine that approaches such as the SIMCA pattern recognition program.

i) The sample must show a specific pattern similar to an Arochlor or mixture of Arochlors,

ii) An externally run standard of a 1:1:1 mixture of Arochlors 1242:1254:1260 is used for quantification. This calibration standard is at a concentration of approximately 100 ng/mL per Arochlor,

iii) Eight of the most significant peaks are chosen from each of the Arochlors (Total 24 peaks),

iv) A minimum of 4 of the 8 peaks must be present to confirm the presence of an Arochlor,

v) A minimum of 3 of these peaks are averaged and are used for quantification,

vi) If any sample peaks are proportionately greater in peak height than what appears in the 1:1:1 mixture, the sample peak is not used for quantification,

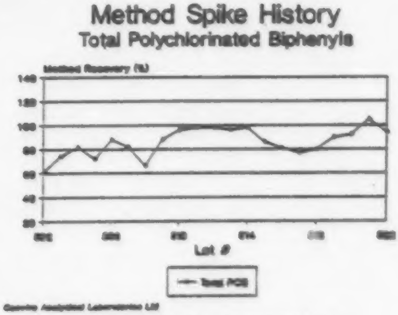
vii) Total PCB's is reported as the summation of the concentrations reported for each Arochlor.

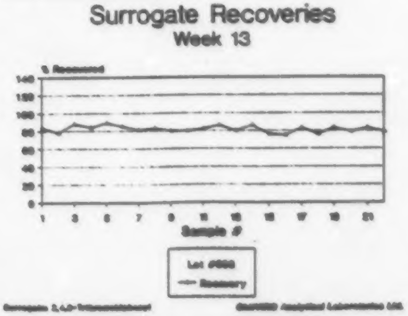
Quantitation is performed by an Internal Standard Method using a pre-injection spike of D10-Anthracene directly into the extract. All data entry to the Ministry of the Environment is made via modem into MOE's Laboratory Information System (LIS).

Quality Assurance / Quality Control:

Incorporated into the QA program is procedures to monitor and document:

1) daily instrument sensitivity
2) laboratory method blanks
3) laboratory method spikes
4) percent recovery of the pre-extraction spike surrogate 2,4,6-Tribromobiphenyl for each extract
5) MOE blind spike acceptance program for any new extraction personnel





In conclusion the confidence in analytical data is becoming evermore important. GC/MS has proven to be a sensitive, selective, highly reliable and highly rugged method of analysis.

Many thanks to Dr. David Hall and his staff of the Drinking Waters Section at the Ministry of the Environment's Rexdale Laboratories.

D6

Evaluation of Environmental Sources of Polychlorinated Biphenyls using Chemometric Methods.

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A number of chemometric techniques were applied to the interpretation of congener-specific high-resolution gas chromatography analyses of polychlorinated biphenyls (PCBs). The numerical techniques employed included SIMCA 3X pattern recognition, principal components analysis, and KNN (K-nearest neighbor statistical analysis). The objectives of the study were to identity, classify, and categorize environmental PCB samples. It was found that the quantitative compositions of commercial Aroclor PCB congeners allow for identification of Aroclor mixtures (such as Aroclors 1221, 1232, 1242 etc.) in environmental samples. Knowledge of the Aroclor composition of water, sediment, and biota samples facilitates assessment of environmental origins and environmental degradation patterns.

Introduction

This paper presents several numerical techniques which allow for the tracing of environmental sources of PCBs, and interpretation of how PCB profiles are altered as a result of introduction into the ecosystem. All of the PCBs that were produced in North America came from a single manufacturer, the Mosanto Chemical Company in the United States. The various technical mixtures provided to industry by this company were given the trade name Aroclor, and were designated according to the chlorine content in the biphenyl molecule. This chlorine content varied from 21% to 68% chlorine by weight. The PCB mixtures produced by this company consist of only a relatively small number of specific grades of Aroclors. These included Aroclors 1221, 1232 1016, 1242, 1248, 1254, 1260, 1262, and 1268, where the last two digits indicate the percentage of chlorine. These commercial products were analyzed by the manufacturer, and variations in the chlorine content were usually adjusted with higher or lower chlorinated products to obtain an average value as specified for a particular Aroclor. Consequently, variations in PCB isomers were significant between batches. However, conger group variations were less pronounced.

Experimental

Sediment, water, and biota samples were collected from Wheatley and Hamilton harbours. Sediment samples were collected by Eckman dredge, water samples were collected by a Van Dorn water bottle. Physa integra (snail), Zonitoidus arborens, Lymnaea stagnalis (snail), pumpinkseed sunfish (Eupomotis gibbosus) (Lepomis?), and Isopods were collected from the nearshore and offshore areas.

Open tubular column gas chromatography analyses were performed on the water, sediment, and biota samples. A Varian Model 6000 GC equipped with a cold on-column injector and an electron-capture detector were utilized. Peaks were identified by a method of relative retention time matching. Decachlorobiphenyl was used as a reference peak. Relative retention time values for the PCB congeners were calculated as the ratio of the individual peak retention time to that of decachlorobiphenyl. The samples were quantified using calibrated Aroclor standards in a 1:1 mixture.

Interpretation of results

Typical chromatograms of commercial Aroclors are given in the figure 1. These chromatograms are the result of the analysis of Aroclor standards obtained in ampoule form from the US-EPA in Cincinnati, Ohio. The various congener groups are indicated by integer numbers on the chromatograms. There is a very noticeable change in the proportion of the PCB congener groups from lower to higher chlorinated Aroclors. It readily becomes apparent that visual inspection of isomer or even congener group patterns from sample chromatograms is extremely tiresome and prone to errors when the objective is to evaluate which Aroclor mixture is present in an environmental sample. This is greatly complicated by the two facts : (1) Many industrial applications of PCBs involved two or more mixtures of Aroclors, and (2) The introduction of PCBs into the environment results in some modification of the isomer and congener group patterns due to various physical, chemical, and biological fractionation mechanisms.

If the composition of the chlorine content of the Aroclors were represented as percentages of the various congener groups, such as in table 1 , the evaluation of PCB profiles would be considerable simplified. This manner of presentation is also convenient for input into many numerical or statistical programs. Some industrial PCB applications are actually mixtures of two or more Aroclors. Industrial mixtures may include binary mixtures composed of two Aroclors, ternary mixtures composed of three Aroclors, and even quaternary mixtures composed of four different Aroclors. Such theoretical industrial PCB mixtures can be numerically approximated by manipulation of the Aroclor end- members (Onuska et. al., 1985).

The results from the analysis of PCBs in the water samples (table 2) from the two harbours revealed that the more chlorinated PCB congeners were present in higher proportions in Hamilton Harbour. Total PCB concentrations were approximately the same for both harbours. However, all water samples contained levels of PCB over the MOE objective for the protection of aquatic habitats which is 1 ug/L.

The sediment results (table 3) exhibit more pronounced variations in the PCB loadings for the two harbours. Once again the more chlorinated congeners are more prevalent in the Hamilton Harbour samples. However, the PCB concentration in the Hamilton Harbour sediment ranged to approximately 10 times that of Wheatley Harbour. The PCB levels in the sediment samples were alarmingly high, especially station 3 in Hamilton Harbour which displayed 14.2 mg/Kg of total PCB.

Concentration patterns of PCB congeners were similar in all types of biota for the two harbours (table 4) with the exception of the Oligochaete worms. This is possibly due to the heterogeneous nature of the offshore area of Hamilton Harbour (with respect to the nearshore area) from which the oligochaete worms were sampled. Whereas the smaller Wheatley Harbour is more homogeneous.

A supervised learning technique was applied to both the theoretical Aroclor mixtures discussed above, and the actual environmental sample results. In the supervised learning approach advance knowledge of sample category or membership is used to train a computer program as to how best to classify unknown samples. Three principal components were extracted from a dataset containing either the Wheatley or Hamilton Harbour data plus the EPA Aroclor standards.

Hamilton Harbour

A plot of the first two components for Hamilton Harbour reveals that the sediment and biota samples appear to plot together in a bunch delineated by Aroclors 1254, 1260, 1262, and 1248. A somewhat separate group includes the two water samples. It is interesting to note that the water sample obtained from the middle of the water column plots near the Aroclor 1248 point; whereas the water sample obtained from the water collected near the bottom plots closer to the sediment and biota samples. Due to the low solubility of PCBs in water, it is possible that the PCB congener profiles observed in the water samples are somewhat depleted with respect to the more highly chlorinated groups, alternately one could assess the water PCB profile as representing the least degraded or modified PCB samples, and as such, more representative of the original source of PCB contamination Hamilton Harbour. If so, the sediment samples indicate that a fractionation mechanism may be responsible for modifying the PCB profile so that the more highly chlorinated congers are preferentially retained within the sediment.

Wheatley Harbour

The plot of the Wheatley Harbour data is similar but not identical to the Hamilton Harbour data. As before, two groupings can be observed, one corresponding to water samples, the other containing the sediment and biota samples. However, the two water samples plot much closer together that they did in the Hamilton Harbour dataset. The sediment/biota samples also plot more closely together then they did in the Hamilton Harbour dataset. This could indicate that the PCBs present in Wheatley Harbour have less diverse origins than PCBs found in Hamilton Harbour. This seems likely as Hamilton Harbour has a diverse industrial base with several possible sources of PCBs. PCBs found within Hamilton Harbour could originate from various steel industry sources, incinerator emissions, and other industries, whereas the only industry found at Wheatley Harbour is related to commercial fishing.

Once again the water samples plot closer to the lower chlorinated Aroclor groups, and the sediment/biota plot closer to more highly chlorinated groups. The sediment/biota sample plot closer to Aroclor 1254 than did the Hamilton Harbour samples. The sediment/biota samples also plot further away from the more chlorinated Aroclors 1260 and 1262 than was the case with the Hamilton Harbour samples.

Because of the limited amount of industry present in Wheatley Harbour, the possible sources of PCB contamination are rather limited. The major source of PCBs in Wheatley Harbour is likely to be PCBs which arose from paints applied to fishing boats. PCBs used to be added to paints as softening or plasticizing agents. It is known that the Aroclors added to paints were a mixture of 1248 and 1254. The conclusion that these paints are the source of environmental PCBs at Wheatley Harbour appears to be borne out by the principal components plot. All samples plot between limits derived by these two Aroclor groups, with little deviation towards the other Aroclors (which is unlike the Hamilton Harbour dataset). Only a small amount of partitioning between the higher/lower chlorinated Aroclors appears to have taken place in the Wheatley Harbour samples.

As mentioned previously, the industrial base of Hamilton Harbour precludes an easy assessment of PCB source material. It appears that four or five different Aroclors may be represented in the Hamilton Harbour dataset. These include Aroclors 1254, 1260, 1262, 1248, and possibly 1242. PCBs in transformer fluid are frequently mixtures of Aroclors 1242, 1254, and 1260. These mixtures often did not contain Aroclor 1248. It is possible that a mixture of these three Aroclor end members would produce points which plot near the observed data points (and also near Aroclor 1248). It is known that the steel industry used to coat steel products with PCBs during the finishing process. These PCBs often consisted of the less chlorinated Aroclor groups. These Aroclors ranged from Aroclor 1016 to Aroclor 1242. It would seem that either these PCBs were not introduced into the Harbour, or have since degraded to appear as the more highly chlorinated forms.

Summary

It was found that the quantitative compositions of commercial Aroclor homologue groups allow for quantification of binary, ternary, and quaternary Aroclor mixtures. Knowledge of the Aroclor technical mixture composition of environmental PCB samples facilities assessment of environmental origins. Modifications to PCB profiles, as a result of environmental degradation, can also be evaluated using similar numerical techniques. These techniques have been applied to PCB samples obtained from sediment, water, and biota from Wheatley and Hamilton harbours.

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Table 1. Composition of Individual Homologue Groups in Selected Aroclors

AROCLOR	1248	1254	1260	1262
Monochloro-	0.0	0.0	0.0	0.0
dichloro-	1.0	0.0	0.3	0.4
trichloro-	28.3	0.3	0.6	1.0
tetrachloro-	54.6	15.0	0.7	0.7
pentachloro-	11.4	44.1	8.0	2.4
hexachloro-	2.6	35.1	42.0	25.5
heptachloro-	1.4	4.6	35.6	43.5
octachloro-	0.6	0.8	11.8	24.3
nonachloro-	0.1	0.1	0.9	2.2
decachlorobiphenyl	ND	ND	0.1	0.5

Table 2. Residues of PCBs in Water at Two Harbours (ng/L)

PCB-homologues	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Total
HAMILTON HARBOUR :							
Station 1	39.1	68.8	69.7	24.4	10.3	2.4	214.7
Station 2	26.3	33.3	18.8	5.0	1.6	1.0	86.0
WHEATLEY HARBOUR :							
Station 1	36.2	148.5	91.0	13.0	2.3	0.1	291.1
Station 2	13.9	35.9	27.3	7.4	1.8	0.1	86.4

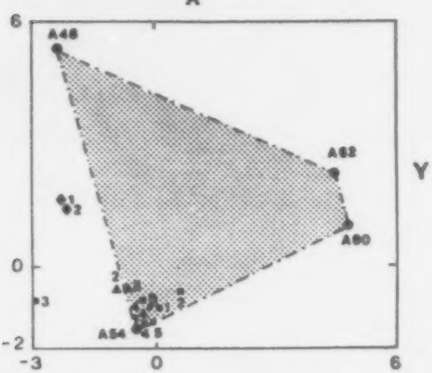
Table 3. Distribution of PCBs in Sediments (μg/kg)

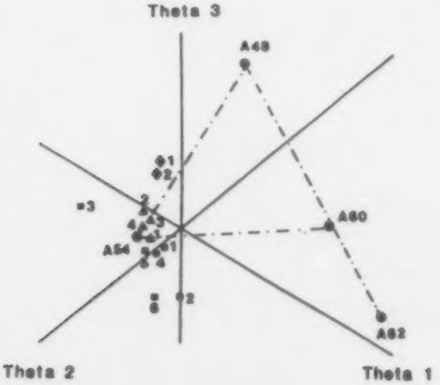
Homologue	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Total
HAMILTON HARBOUR								
Station 1	97.4	134.9	324.6	284.5	30.9	70.9	5.3	948.5
Station 2	41.0	72.4	174.3	140.3	146.2	31.4	2.3	608.0
Station 3	733.0	1065.0	3321.0	3289.0	4044.0	985.0	748.0	14185.0
Station 4	235.7	451.0	777.5	451.3	462.7	112.0	8.8	2499.0
Station 5	205.9	441.6	724.8	443.6	350.5	75.8	6.1	2248.0
Station 6	148.4	267.4	825.6	744.2	865.1	206.3	15.8	3073.0
WHEATLEY HARBOUR								
Station A	28.8	111.2	474.0	358.0	175.8	26.6	2.4	1176.8
Station B	5.6	20.0	67.8	51.0	16.8	2.0	2.8	166.0
Station C	14.8	64.6	252.2	140.8	91.6	14.6	1.4	580.0
Station D	5.8	30.8	103.2	53.0	31.2	5.6	0.4	230.0
Station E	5.6	34.0	155.4	110.0	40.2	5.8	0.1	351.1
Station F	21.4	54.2	189.8	132.2	59.6	7.7	0.5	465.0

Table 4. Distribution of PCBs in Biota (µg/kg wet weight)

Homologue	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Total
HAMILTON HARBOUR							
Isopoda	16.7	32.2	37.9	17.5	5.3	ND	109.6
Physa integra	5.5	36.5	71.2	32.0	12.0	1.1	158.3
Oligochaetes	32.6	39.5	54.5	45.3	30.5	4.8	207.2
WHEATLEY HARBOUR							
Fish (*Eupomotis gibbosus*)	7.0	10.3	26.5	21.6	3.9	ND	69.3
Zonitoidus arborens	5.1	17.3	64.8	46.3	16.3	1.6	151.4
Physa integra	5.6	14.3	27.9	21.2	3.1	ND	72.1
Oligochaetes	22.4	40.2	102.8	72.2	22.6	2.5	262.7
Lymnea stagnal.	1.2	7.4	22.7	24.5	2.9	ND	58.7

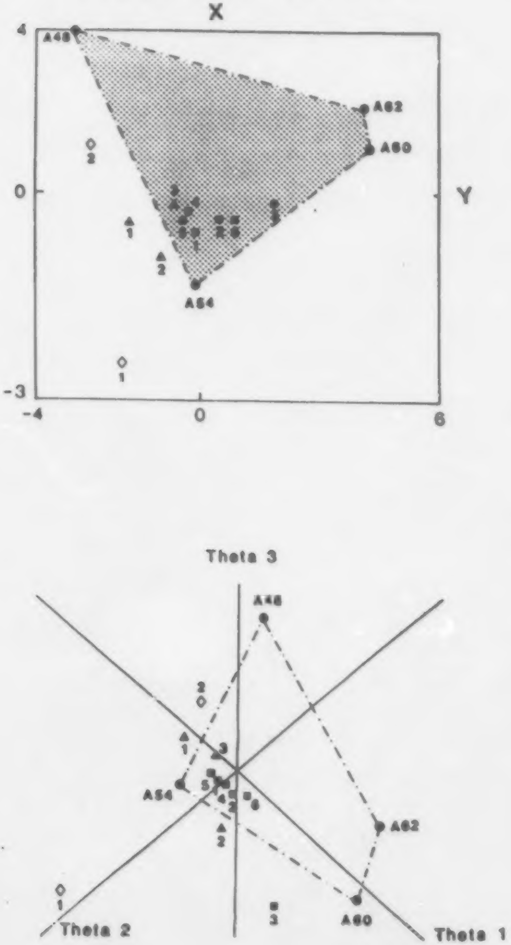
WHEATLEY HARBOUR





Water (◆), Sediment (■), and Biota (●)

HAMILTON HARBOUR



Water (◆), Sediment (■), and Biota (●)

D7

ISOLATION AND DERIVATIZATION OF CHLORO-AROMATIC ORGANIC ACIDS ON SOLID SUPPORT

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INTRODUCTION:

Gas chromatographic determination of the chlorophenoxy acetic acid (ClPAA's) herbicides and the breakdown products ie the chlorophenols (ClP's) from water requires that analytes first be isolated from matrix and then derivatized at the acidic functionalities. Reaction with pentafluorobenzyl bromide (PFBBr) (1) or methanolic BCl$_3$ (2), or silylation (3) with cyano containing reagents and with have been used to prepare the derivatives for gas chromatographic determination of parent herbicides and the corresponding phenols. Standard EPA procedures are based on derivatization with PFBBr but the process is complex and involves use of toxic catalysts such as crown ethers (1). The appropriate use of solid supported processes (4-6) could be used to simplify such procedures and eliminate the use of toxic materials in the analytical laboratory. Ideally these processes on solid supports should include both adsorption and derivatization.

We investigated the simultaneous adsorption and pentafluorobenzylation of ClPAA's and ClP's on solid supports directly from 5-20 ml of water in order to determine if this simplifying technology could be applied to environmental problems. Electrophoric and water insoluble pentafluorobenzyl (PFB) derivatives suitable for gas chromatography were via reaction with PFBBr supported on XAD-2 (7-12).

While simultaneous isolation/derivatization was facile there was also a simultaneous production of the PFB esters of fatty acids that are a common contaminant of glassware and all samples that have biological materials in them (e.g. cells, cellular debris). These interfered with determination of the analyte and resulted in a high detection limit. Moreover, the reaction rate for derivatization from 20 ml of water was slow.

Several modifications of the procedure were investigated to alleviate these problems. First an in-line chromatographic separation of derivatized analytes from interferences was developed (14,15) to separate fatty acids from the PFB ester of 2,4-Dichlorophenoxy acetic acid (2,4-DiClPAA). Second benzyl (Bz) esters were prepared. Since Bz esters of the fatty acids were not electrophoric whereas Bz derivatives of the halogenated target analytes were readily detected by the electron capture detector this derivatization procedure was expected to reduce the interferences (15). Finally, extraction from large volumes was investigated in order to increase the amount of analyte relative to the interferences generated from the fatty acids in the background. Due to the concentration of analyte on the resin, it was possible to test different methods of forming the Bz and PFB derivatives on the resin.

EXPERIMENTAL:

Apparatus: The derivatives of the analytes were determined on a Helwett-Packard (H-P) 5710 or 5790 gas chromatograph equipped with a pulse linearized electron capture (ECD). The 5710 instrument was equipped with a 15 m DB-1 megabore column with an inner diameter of 0.53 mm and a film thickness of 1.5 micrometers. The 5790 instrument was equipped with a 30 m DB-1 J & W fused capillary column with an inner diameter of 0.32 mm and a film thickness 0.25 micrometers. The output of the detectors was monitored on H-P 3390A recording integrators. Hydrogen was used as a carrier gas for the megabore column the flow rate was set at 4 mL/min and for the capillary column it was set at a linear velocity of 62 cm/sec at 180°C and 10 % methane in argon was used as a make-up gas at a flow rate 15 ml/min.

Reagents: Pentafluorobenzyl bromide and BzBr were purchased from Caledon Laboratories, Georgetown, Ontario, and from Aldrich Canada respectively. The macroreticular resin, XAD-2, a cross-linked copolymer of styrene/divinylbenzene was obtained from BDH Laboratories, Toronto, Ontario and was cleaned and stored as previously described (13). Florisil, basic alumina, disposable 1 ml Supelclean columns for semi-preparative chromatography and a vacuum module were also purchased from Supelco (Canada) Oakville Ont. Solvents were purchased from the usual commercial suppliers, such as Fisher, BDH and Aldrich Canada. Pure analytes were obtained from the E.P.A Repository.

All the glassware was silylated by standard procedures. Glassware and plasticware was washed with methylene dichloride, methanol, acetonitrile and dried prior to use.

Preparation of PFB and Bz Derivatives: Derivatives of the pure analytes were prepared by stirring of the organic acid in acetone with PFBBr or BzBr with K_2CO_3 as the base. Reaction work-up consisted of evaporating the acetone, extracting the residue with CH_2Cl_2 and finally washing the organic phase with distilled water. The PFB products were purified by thin-layer chromatography.

Derivatization and Isolation: Three hundred mG of XAD-2 was added to glass 25X200 mm screw cap vials and wetted with 300 µl of acetonitrile. The vials were charged with 40 mL unbufferred tap water containing C^{-14} radiolabelled 2,4-DiClCPAA and corresponding to 5 nG/ml. The aqueous phase was acidified with 0.1 N HCL and the reaction mixture was shaken for 30 minutes. The resin was isolated by filtration in a 5 mL Supelclean cartridge. The PFB or Bz ester was formed via one of two alternative procedures.

In the first the resin was transferred to a 16X100 mm screw-cap vial. The reaction was initiated by adding 150 µl of a 9/1 (v/v) solution of PFBBr or BzBr in hexane and the reaction mixture was agitated by ultrasonication at 40°C. The resin was isolated by filtration into a 5 ml supleclean cartridge and was washed with distilled water which was removed by suction. After removal of bulk water by filtration, the resin was dried by the addition of a water scavenger, 100 µL acidified 2,2-dimethoxypropane (DiMP) and allowed to remain in contact with the resin for 15 minutes (14,15). Excess scavenging reagent and products of hydrolysis (acetone and methanol) were removed with a slow stream of nitrogen at room temperature.

In the second procedure derivatization procedure, after the adsorption step, the resin was dried by the addition of DiMP as described above. Two hundred µl of a 1/19 solution of PFBBr or BzBr in CH_3CN containing 10 µl of Di-Isopropyl Amine (DiPEA) was added and the reaction mixture was allowed to stand at room temperature for 15 min. The solvents were then evaporated at 40°C with a stream of nitrogen.

For the purification of the PFB ester cartridge containing the dried XAD-2 was then inserted linked in series to a 1 mL cartridge containing Florisil which was in turn was linked to a silica gel column of similar dimensions. Elutions were carried out using a Supelco Vacuum module. The 2,4-DiClDPAA-PFB ester was eluted with 30 mL 25% toluene in hexane to elute the fatty acid PFB esters and 30 mL 50% CH_2Cl_2 in hexane to elute the PFB ester of 2,4-DiClPAA.

For isolation of 2,4-DiClCPA Bz ester the cartridge with the XAD-2 was simply linked to a column of florisil. The linked system was washed with 24 mL hexane followed by hexane/ toluene (95/5 v/v). The 2,4-DiClCPA Bz ester was eluted with 50% hexane/ CH_2Cl_2.

Gas Chromatography: Samples were analyzed by gas chromatography with electron capture using the columns described above. For the capillary column the following temperature conditions were used: 170-215°C at 4°C/min; 215°C to 300°C at 20 °C with a 2 minute hold at 300°C. For the megabore the initial temperature was 170°C, the rate of increase was 4°C and the final temperature was 290°C. There was no delay at the initial or final temperatures.

Calculation of Yield and Reaction Rate : Yield of the reaction was calculated based on the recovery of radiolabel when the reaction was carried out with C^{14} 2,4-DiClPAA. The PFB derivative, but not the parent carboxylic acid, eluted from the chromatographic systems described above; acccrdingly the recovered radiolabel represented the yield of the reaction for carboxylic acids. The reaction rate was calculated form the rate of disappearance of the radiolabel from aqueous solution.

RESULTS AND DISCUSSION:

Under the described conditions, adsorption of 2,4-DiClPAA from 40 ml volumes was time dependent with a half life of 8 minutes. Thus effective adsorption onto a resin bed of 300 mG required 30 minutes. This slow rate of adsorption due, in part, to the hydrophilicity of the analyte but also the high ratio of liquid to solid phase. Once the analyte had been adsorbed the resin was isolated and two different reaction techniques were investigated.

In the first technique ultrasonication was used to agitate the solution. Since the resin with the adsorbed analytes was isolated the ratio of liquid to solid could be adjusted at will and kept as small as required. Both PFBBr and BzBr were used for the derivatization. In a reaction time of two hours the yield of the PFB ester was 60%. As in previous studies the reaction yield for Bz ester lower (40%) since BzBr is less reactive than PFBBr. These are comparable to those obtained by shaking; although it is interesting that the reaction rate for derivatization with BzBr appears to be faster than that using the classical agitation technique (14,15). Use of ultrasonication has a particular advantage - capping is not required as tubes can be left open to the atmosphere and in a vertical position. This removes one step from the procedures, eliminates the need for teflon lined caps and losses due to leaking tubes if the seals are not set properly. It would be particularly advantageous for development of automated techniques where capping would be a problem.

In the second technique it was possible to take advantage of the fact that in previous work we had demonstrated a chemical drying technique using acidified DiMP (14,15) as a water scavenger. Since after adsorption the resin was saturated with acidified water the surface could be dried simply by adding the neat reagent with the adsorbed water supplying the required proton to catalyze the conversion of DiMP and water into methanol and acetone. Once the surface was dry the PFB ester was formed via base catalyzed esterification - a reaction that requires anhydrous conditions. This was carried out simply by addition of a solution of PFBBr and DiPEA in CH_3CN. limiting the volume of this solution to the pore volume of the resin there was little loss of analyte from the surface. Since there was no water to protonate the highly hindered base the acid 2,4-DiClPAA was ionized in-situ and was thus derivatized. In this procedure the resin functioned simply as a support for the analyte, reagent and base. The reaction rate under these conditions is considerably faster and even for BzBr a yield of 47 % was obtained in 15 minutes.

The in-line chromatographic clean-up eluted 80-90% of the PFB esters of the fatty acids in the 25% toluene/hexane fraction. The

50 % CH_2Cl_2/hexane fraction eluted all of the PFB ester 2,4-DiClPAA and the remaining PFB esters of fatty acids. (Figure 1). Despite this 400% enrichment in derivatized analyte a more substantial reduction of interference was required.

Glassware is one source of the fatty acids and a procedure described by Greving et al was used (16) was used to clean the glass reaction vessels. This produced approximately a 50% reduction in the fatty acid PFB esters. If an attempt was made to silylate these tubes again the contamination increased to levels found in glass-ware prepared by standard methods i.e. acid washed and silylated (Table 1).

Table 1: The effect of treating glassware on the amount of background fatty acids recovered.

Treatment of glassware	Fatty acid PFB ester	Ratio of Response Relative to External Standard
Clean with Decon, Wash with Dilute HCl, Silylate	Dodecanoic	1.2
	Tetradecanoic	1.4
	Hexadecanoic	2.8
	Octadecanoic	3.1
Treat with Acidified Hydrogen Peroxide	Dodecanoic	0.6
	Tetradecanoic	0.6
	Hexadecanoic	1.5
	Octadecanoic	1.9
Treat with Acidified Hydrogen Peroxide; Silylate	Dodecanoic	1.3
	Tetradecanoic	1.1
	Hexadecanoic	3.2
	Octadecanoic	2.9

Thus cleaning of glassware only partially reduces the background; the remaining fatty acids are possibly present on the resin or in the reagent. In addition, any further treatment of the glassware results in an increase in the amount of fatty acids. It must however be expected that in environmental samples the fatty acid concentration could be quite high and in addition plasticware used in sample preparation can also contribute interferences (17). Thus simply cleaning laboratory equipment will only partially resolve the problem and a more generic solution to the background problems are required.

Formation of the Bz rather than the PFB ester produced some improvement in the background. The reaction rates for this reaction were slower than for pentafluorobenzylation. In addition, the limitations to sensitivity arose from contaminants of plasticware particularly from low levels of PFB esters that was due to reuse of the cartridges.

SUMMARY: Pre-adsorption of analytes can be used to simplify the procedure by the allowing agitation of an aqueous reaction mixture by ultrasonication. In addition the use of a chemical drying procedure allows of XAD-2 as a support for a base catalyzed reaction. Interferences can partially reduced by in-line chromatography or by treatment of glass-ware with oxidizing agents. The latter approach can only reduce those interferences present in the laboratory; the former approach using more sophisticated instrumentation would reduce those interferences from fatty acids that must be present in the environment.

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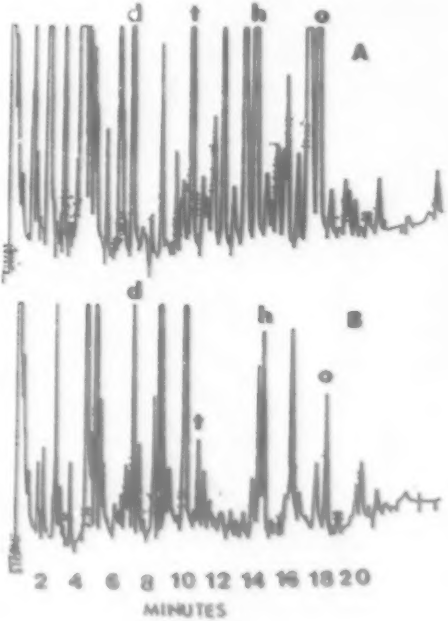
Figure 1. GC/ECD traces of eluates from the XAD-2 reactor bed - Florisil - Silica Gel link: A) fatty acid fraction and B) chlorophenoxyacetic acid fraction. Peak corresponding to PFB ester of 2,4 Dichlorophenoxy Acetic Acid is darkened.

PFB esters of: d = dodecanoic acid; t = tetradecanoic acid; h = hexadecanoic (palmitic) acid; o = octadecanoic (stearic) acid.



D8

BIAS DUE TO SAMPLING GROUNDWATER AND SURFACE WATER FOR TRACE ORGANIC CONTAMINANTS. Part I. Losses Due to Volatilization.

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INTRODUCTION

Contamination of surface and groundwater by synthetic organic compounds is a major environmental concern in Ontario and most industrialized areas. In sampling natural waters for organic contaminants, two main sources of negative bias are recognized, loss of volatile compounds by partitioning into the atmosphere and loss of hydrophobic compounds by sorption onto synthetic polymers used in the construction of wells and samplers. Considerable research has been conducted at the Waterloo Centre for Groundwater Research and by numerous other research groups into the magnitude and the means to minimize these biases.

It is generally recognized that compounds with Henry's law constants greater than 0.001 (atm m^3 / mol) have the potential to be volatilized if the solution is exposed to the atmosphere during sampling and analysis. Most common organic groundwater contaminants fall into this category, and evaluating the potential for volatilization loss has been the object of several groundwater sampling studies. Barker and coworkers [1,2] evaluated the potential for volatilization and sorption losses when using multilevel piezometers and several other sampling devices. Ho [3] studied the effects of transport line material, pumping rate and sample lift height on the recovery of volatile organics in water with a peristaltic pump. Barcelona et al [4] tested a large number of samplers in an attempt to evaluate the effectiveness of various sampling mechanisms. Pearsall and Eckhardt [5] evaluated several common samplers and the effects of variations in sampling procedures and details of set-up. These studies have demonstrated that: 1) the potential for significant negative biases exists with common sampling devices, 2) the biases appear to be caused by volatilization (and by sorption in some cases), and 3) some consistency among studies has been found in the relative effectiveness of various samplers and sampling mechanisms.

Recently, particular emphasis has been placed on the problem of sampling gas-charged groundwater such as can be encountered in landfill leachate plumes and natural gas associated formations, for example. Pankow [6] provided a theoretical basis for estimating the artifacts due to bubble formation during sampling. Barker and Dickhout [2] tested the effectiveness of a positive displacement pump, an inertial lift pump and a peristaltic pump in sampling gas-charged water for volatile organics. Their finding that the peristaltic pump induced the greatest negative bias qualitatively agrees with theory; however, a consistent correlation between relative loss and Henry's constant was not observed, although only a narrow range of volatilities were represented by the compounds used.

It is evident that further research is required to realize the goal of quantitative estimation of sampling bias due to volatilization. The present study incorporates several improvements in design over the previous study by Barker and Dickhout [2]. Larger Henry's constant values are represented by the organic contaminants, and methane was included. Dissolved carbon dioxide concentrations were measured in order to establish a link with theory. In addition, the experimental well was constructed of stainless steel instead of PVC, eliminating the possibility sorption losses in the well; the well contained a sampling port at the bottom for obtaining representative control samples. Finally, six samplers were evaluated at two concentration levels, making this a more comprehensive study.

METHODS

An artificial well was installed in a stairway at the University of Waterloo Centre for Groundwater Research. The well essentially consisted of a 6 " diameter stainless steel pipe, 32' in height with a sampling port located near the bottom. The well was filled and drained at the bottom with an air-driven pump connected to a stainless steel reservoir. Gas-laden artificial groundwater, approximating that in an aquifer contaminated by low-level organics, was made as follows. A 90 litre volume of tap water containing 3.4 g/L sodium bicarbonate was prepared in the reservoir and its pH was adjusted to 9.0 with 1 N NaOH. The water in the reservoir was spiked with: 1) a saturated solution of methane in water, and 2) a methanolic stock solution containing benzene (366.5 ppm), toluene (723.3 ppm), trichloroethene (610.7 ppm), trans-1,2-dichloroethene (262.1 ppm), and 1,1-dichloroethene (254.0 ppm). The spiking volumes that were used in the experiments are given below.

Experiment	Concentration Level	Volume (mL)	
		Methanolic Stock	Methane Water
1-2	high	9.00	4000
1-1	low	0.45	415
2-2	high	9.00	4000
2-1	low	0.45	415
3-2	high	9.00	4000
3-1	low	0.90	1000
4	high	9.00	4000

After stirring, the solution in the reservoir was pumped through a port in the bottom of the well along with 2 L of a 10 % HCl solution, thus converting the bicarbonate ions to carbon dioxide. Since the bicarbonate and HCl solutions were proportionally mixed as they entered the bottom of the well, some of the carbon dioxide was liberated, but most was kept in solution by hydrostatic pressure in the well.

The following sampling systems were evaluated: a double check-valve stainless steel bailer (BAIL), a peristaltic pump (PER), a WaTerra inertial pump (WAT), an IEA syringe sampler (SYR), a Well Wizard bladder pump (WIZ), and a Solinst double-valve purge/sample pump (SOL). In each experiment, the high capacity foot-valve WaTerra (model D-32) and one or two other samplers were tested, and the water was sampled using the control port at the bottom of the well. In experiment 4, the high capacity WaTerra was compared with the smaller WaTerra (model D-16). Approximately the same well depth was sampled by all of the samplers.

Five replicate samples were taken with each sampler and from the control port. Upon collecting a sample, two 60 mL hypovials were immediately filled to overflowing and capped with teflon-faced septa. The hypovials were stored underwater at approximately 4 C and the contents were analyzed within five days. The organic contaminants (benzene, toluene, TCE, 1,2-DCE, 1,1-DCE) were determined using one of the hypovials from each pair, and the other was used for determining the methane and carbon dioxide concentrations. The organic contaminants were determined in the headspace created in the hypovials when 15 mL of of sample was replaced with an equal volume of laboratory air. After equilibration, the headspace was injected directly into a gas chromatograph fitted with a photoionization detector. Methane and carbon dioxide were also determined by static headspace gas chromatography with FID and TCD detectors. The relative standard deviations for five replicate determinations of the gases and the organic contaminants ranged from 4 to 8 %.

RESULTS

The data are summarized by experiment in Table 1, which gives the average concentrations for each group of five replicate samples. Percentage losses were calculated from the data of Table 1 by the formula

$$Loss(i,j,k) = -100 \times (Sampler(i,j,k) - Control(i,j)) / Control(i,j)$$

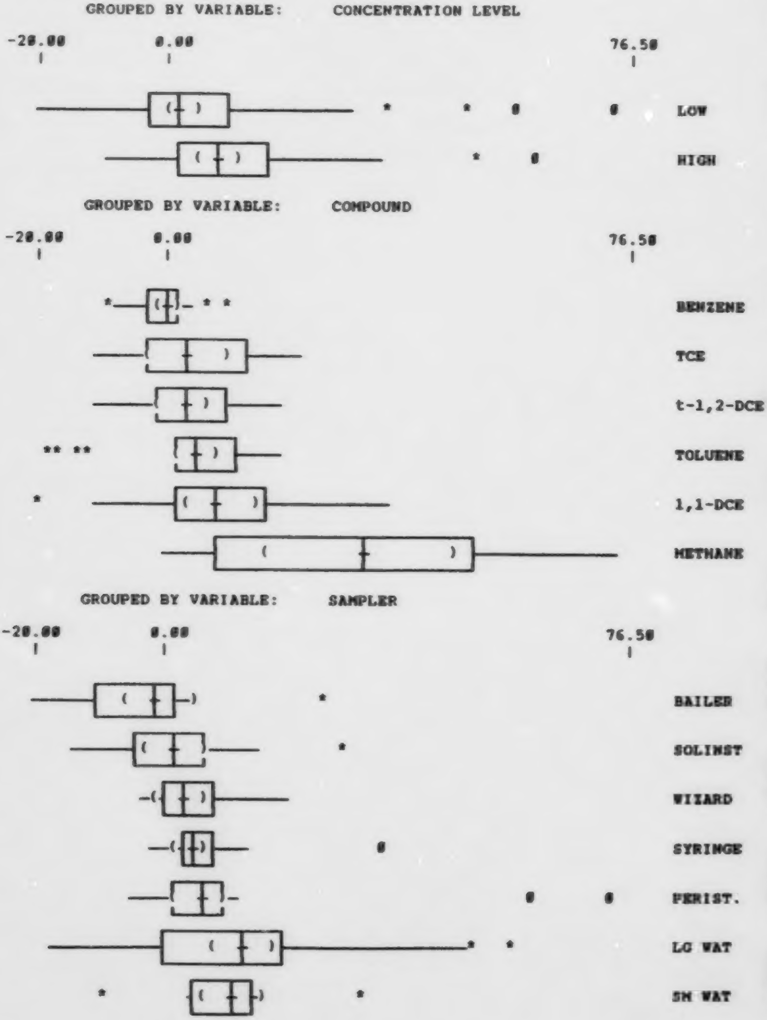
Sampler(i,j,k) is the mean concentration for compound i, concentration level j, and sampler k. Similarly, Control(i,j) is the mean concentration for the appropriate control sample. The percentage losses have been analyzed by the box plot technique [7]. In making statistical comparisons, a significance level of 0.05 is used throughout. Figure 1 depicts the percentage losses obtained by one-way classification according to compound, sampler and concentration level. Significantly positive biases are notably absent in all three categories. The difference in bias between the high and the low concentration levels is barely significant, with the high concentration bias being about 6 % more negative than the low concentration bias. The percentage loss incurred at the low level is not significantly different from zero. The percentage of compound lost by volatilization should not be affected by the concentration of the compound [6].

Considering next the box plots for the organic compounds, methane shows the greatest median loss, and this is significantly greater than the medians for the other compounds. Methane also shows a significantly greater variance. The methane losses are significantly correlated with the CO_2 losses (Figure 2), which suggests that volatilization is responsible for the methane losses. The other compounds are not significantly correlated with CO_2, and this is consistent with the fact the Henry's constant for methane is larger than those for the other compounds. The Henry's constants (atm m^3 / mol) for the compounds are [6]: methane, 0.676; 1,1-dichloroethene, 0.19; t-1,2-dichloroethene, 0.067; trichloroethene, 0.0091; toluene, 0.0067; benzene, 0.0055. The order of increasing loss among the compounds approximately parallels the order of increasing Henry's constant. Most of the variability among compounds is due to the contrast between methane and the other compounds. The 95 % confidence intervals (indicated by parentheses in the box plots) for the other compounds overlap extensively; for three

Table 1. Mean concentrations (N~5) for each experiment. [illegible]centrations are given in 10^{-6} g/L except for CO_2 which is given in g/L.

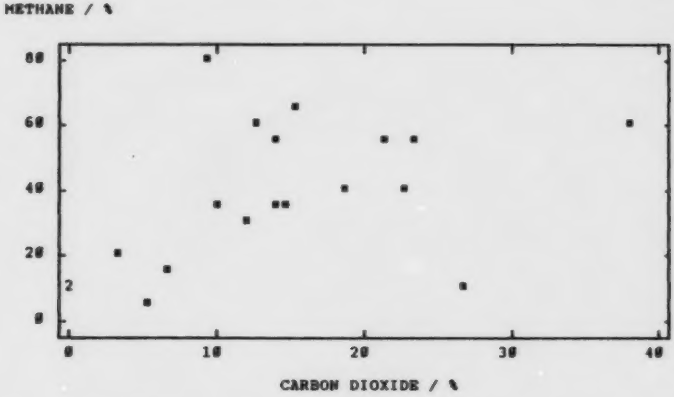
Expt.	Sampler	Compound						
		BEN	TOL	TCE	1,2-DCE	1,1-DCE	METH	CO_2
1-2	CONT	16.8	33.6	26.5	10.8	10.4	408	1.24
	WAT	16.3	31.2	24.0	10.0	9.6	260	0.96
	BAIL	16.0	31.8	25.2	10.5	10.5	292	1.10
	PER	15.8	29.6	23.1	10.1	9.1	153	1.05
1-2	CONT	0.93	1.84	1.39	0.48	0.35	36.5	1.11
	WAT	0.91	2.10	1.42	0.47	0.32	14.6	0.97
	BAIL	0.91	2.14	1.50	0.52	0.42	33.6	0.81
	PER	0.91	1.58	1.42	0.45	0.34	8.6	1.01
2-2	CONT	21.7	42.6	35.3	14.4	13.3	232	1.24
	WAT	19.1	35.3	27.0	11.5	8.8	152	1.06
	WIZ	21.1	39.9	33.1	13.6	11.7	215	1.30
2-1	CONT	1.1	2.13	1.95	0.63	0.45	32.5	1.43
	WAT	0.99	1.98	1.60	0.56	0.37	16.0	1.13
	WIZ	1.1	1.83	1.95	0.55	0.35	31.3	1.35
3-2	CONT	19.4	39.4	29.1	13.6	12.4	426	1.97
	WAT	18.7	33.5	24.6	10.8	9.6	198	1.51
	SOL	20.3	36.6	29.7	12.1	11.2	347	1.90
3-1	CONT	2.13	3.60	3.19	1.09	0.76	95.0	1.94
	WAT	2.14	3.96	2.97	1.11	0.82	38.9	1.19
	SOL	2.11	3.99	3.07	1.04	0.72	64.3	1.66
	SYR	2.0	3.2	3.0	0.92	0.46	86.8	1.96
4	CONT	21.3	38.7	36.3	13.1	11.0	382	1.96
	LG.WAT	20.5	30.2	27.4	10.6	8.85	247	1.59
	SM.WAT	22.7	32.5	30.2	12.0	9.54	248	1.76
	SYR	20.4	36.1	33.9	12.7	10.1	338	1.82

Figure 1. BOX PLOTS OF PERCENTAGE LOSS (N = 108)



of the compounds, the median biases are not significantly different from zero.

Figure 2. SCATTERPLOT OF PERCENTAGE LOSS, METHANE VERSUS CARBON DIOXIDE



The variability associated with sampler bias, expressed as the standard deviation of the medians, is 4.3 %. This is comparable to the analytical variability for replicate analyses of the same sample. The sampling losses increase in the order: BAIL, SOL, WIZ, SYR, PER, WAT. The 95 % confidence intervals overlap extensively, so the order is not well-defined. The losses for the SYR, PER and WAT samplers are significantly different from zero, while those for the BAIL, SOL and WIZ samplers are not significantly different from zero or from each other. The losses for the large and small WAT samplers are indistinguishable from each other and are significantly greater than those for the BAIL, SOL, WIZ, and SYR samplers.

The box plots provide a robust (nonparametric) one-way analysis of variance. A two-way anova is more powerful, because the error mean square is reduced by taking into account the variance due to the other factor, but the experimental data violate the homogeneity of variance assumption. As mentioned previously, methane shows a larger variance. The simpler method of analysis (box plots) was used, because it is less prone to type II error (concluding that a significant difference exists when it does not). The methane data appear as outliers in the box plots for the samplers, thus exerting little influence on the medians and on the 95 % confidence intervals. This was verified by comparing the box plots in Figure 1 with those obtained when the methane data was deleted. The sampler losses depicted in Figure 1 are therefore representative for compounds having Henry's law constants smaller than 0.2 atm m^3 / mol.

The losses for methane indicate a somewhat different sequence for the samplers from that indicated by the other compounds. In order of increasing methane loss, the sampler sequence is SOL, SYR, BAIL, WIZ, WAT, PER. However, a one-way analysis of variance indicates that the sampler means are indistinguishable. Because the degrees of freedom for the test is small, it is not possible to discriminate small differences between sampler means for individual compounds. More replication would be necessary to test hypotheses concerning the relative effectiveness of the sampling devices for particular compounds. This provides some justification for pooling the compounds in the test for sampler effects, and further justification is provided by the fact that biases are not significantly correlated among the compounds, i.e. the assumption of independent errors is not violated.

The percentage losses computed from the data of Table 1 were also used to estimate the random variability associated with sampling. The sampling variability, expressed as a standard deviation, was computed for each compound by taking the square root of the mean square error of a one-way analysis of variance for sampler effects. The high and low concentration data were pooled, yielding 12 degrees of freedom for the estimate. The variablitities for benzene and methane are 4 % and 33 %, respectively, and the middle compounds fall into the range of 11 to 17 %. The sampling variabilities tend to increase as the Henry's law constants increase. Because each datum is the mean of five replicate samples taken with a given sampler in a single day's experiment, the variability for single samples is greater. Assuming that the variability for samples taken on a single day is the same as that for samples taken on different days, the sampling variability for single samples is estimated to be in the range of 20 to 40 % for the middle compounds. Therefore, the systematic variability associated with the samplers (4.3 %) is small relative to the random variability associated with taking replicate samples with a given sampler. It is also worth noting that the sampling device may introduce less bias than the laboratory performing the analysis. This is demonstrated by the results of a recent interlaboratory comparison for the analysis of low molecular weight aromatic compounds, e.g. benzene, toluene, etc. (R. Dickhout, unpublished data). A relative standard deviation of 28 % was obtained for the 10 participating commercial laboratories, and this is considerably larger than the 4.3 % RSD obtained for the seven sampler medians.

DISCUSSION

The question of whether or not volatilization is the mechanism responsible for the observed losses of organic compounds can now be discussed. The fact that methane showed the greatest percentage losses is consistent with the relative magnitudes of the Henry's constants. Most of the variation in the biases for the compounds and in the Henry's constants is due to the contrast between methane and the other compounds. The fact that the methane losses are significantly correlated with the CO_2 losses (Table 1) strongly suggests that methane bias is due to volatilization. Recent sampling studies carried out in this laboratory (R. Dickhout, unpublished data), have revealed that substantial losses occur during the well filling procedure, apparently caused by the effervescesce produced when the sodium bicarbonate and HCl solutions are mixed.

Substantial amounts of carbon dioxide were lost during the sampling process. From the median percentage loss (15 %, Figure 2) and the typical concentration for CO_2 in the control samples (1 g/L, Table 1), it is estimated that about 0.07 mL of carbon dioxide gas was lost to the atmosphere per mL of solution. Pankow [6] has derived equations to predict sampling losses due to spontaneous bubble formation in gas-charged waters. Assuming that carbon dioxide gas bubbles were produced during sampling, Pankow's eq 11 predicts percentage losses ranging from 1.6 % for benzene to 86 % for methane. The predicted losses are, on average, about a factor of 2 greater than the observed percentage losses (Figure 1). However, gas stripping of volatile compounds is not likely to be the mechanism responsible for the observed losses. The estimated in situ gas pressure (fugacity) for dissolved carbon dioxide in the well is 0.68 atm. Spontaneous formation of gas bubbles cannot occur unless the ambient pressure is reduced to a value smaller than the in situ gas pressure plus the vapour pressure of water. The peristaltic pump is the only sampler which could cause a substantial reduction in the ambient pressure. It is therefore postulated that the volatile compounds were lost by mass transfer at the air-water interface. The lack of an exact correlation between percentage loss and Henry's consant value may be due to the possible non-equilibrium nature of the postulated mechanism or due to the fact that the losses were small relative to experimental error.

Because it is a gas at room temperature and pressure, methane has a much greater potential for volatilization than for sorption by synthetic polymers. The other compounds would have greater potential for sorption relative to methane because they are liquids. Interestingly, the order of increasing Henry's constant is similar to the order of decreasing solubility in water for the compounds. A compound's solubility in water is correlated with its polymer-water partion coefficient, so the tendency for sorption losses would be expected to approximately parallel that for volatilization losses among compounds having a narrow range of boiling temperature, which is the case for the liquids used in the experiments. Some of the samplers used in this study expose the sample to synthetic polymers. For example, plastic transfer line tubing was used with the WAT, WIZ, PER and SOL samplers. Exposure to polymeric materials is thought to be minimal for the BAIL and SYR samplers. The order of bias among the samplers does not appear to be correlated with the degree of exposure to organic polymers, however.

The relative performance of the samplers seems to be consistent with the results of previous studies [2,4,5] which show that sampler bias tends to increase in the order: grab samplers, positive displacements pumps, suction pumps (PER). The inertial lift pump (WAT) has not often been included in previous studies. The one published evaluation [2], indicated that the WAT sampler performed as well as the WIZ sampler and better than the peristaltic pump. In the present study, the WAT sampler did not perform as well as the other samplers. This apparent discrepancy may reflect differences in the way the samplers were used in the two studies, since it was previously shown [3,5] that factors such as rate of pumping and sample lift height can influence bias.

The present study has shown that the random variability associated with taking replicate samples is large relative to the variability associated with the different sampling devices. This means that large numbers of independent sampling events are needed to discriminate differences in sampler performance. The previous studies of sampler bias have not in general provided a firm statistical basis for discriminating differences in sampler performance, and the results of the present study are circumscribed by the kind and degree of replication employed and other details of the experimental design. The relative and absolute biases associated with sampling devices in such studies may be influenced by implicit conditions that will require considerably more effort to elucidate.

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D9

POYNUCLEAR AROMATIC HYDROCARBONS IDENTIFICATION

USING GC/FT-IR AND PAIRS

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ABSTRACT

Gas chromatography/Fourier transform infrared (GC/FT-IR) spectra of 33 polynuclear aromatic hydrocarbons (PAHs) have been measured at the Ontario Ministry of the Environemnt. High signal to noise ratio (SNR) vapor phase spectra have been obtained for the majority of the PAHs, a lower SNR being obtained for 4 PAHs with very low vapor pressures. A vapor phase infrared spectral library has been created which makes the identification of PAH target compounds possible by GC/FT-IR. The spectral region 700 to 1000 cm^{-1} containing the C-H and -CH_2 out-of-plane and C-C in-plane bending modes demonstrate a unique spectral feature for each PAH. It is possible to distinguish between a group of PAH isomers using only the information from this spectral region. The PC based version of the program for the Analysis of InfraRed Spectra (PAIRS*) is employed and an interpretation tree specific for PAHs is at the preparation stage to make "functional group frequency" screening of PAHs possible.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are a major class of chemical compounds with extremely complex structures. Due to large variablity in isomer formation several hundred different types of PAHs can exist. For example, for PAH's containing 6 aromatic rings, 82 isomeric configurations are possible. Since the toxicity, carcinogenicity, and mutagenicity of different PAH isomers can be very different, the ability to distinguish these isomers for environmental assessment and consequently, for remedial actions is important. The Ontario Ministry of the Environment (MOE) has been analyzing 37 targeted PAHs at the Trace Organics Section (TOS) of the Laboratory Services Branch (LSB)(1). These PAHs had been selected based on their occurrence in the province of Ontario. The spectra of only 13 of these 37 PAHs are in the Nicolet/Aldrich enhanced U.S. Environmental Protection Agency infrared vapor phase library

(EPA library) (2). The lack of the other 24 PAH spectra in the EPA library complicates the identification of the gas chromatograph/Fourier transform infrared spectra (GC/FT-IR) of these PAHs.

The applicability of gas chromatograhy/ Fourier transform infrared spectroscopy (GC/FT-IR) to environmental sample analysis containing some PAHs has been demonstrated by several groups (3-5). In these studies only a few of the PAHs listed in Table 1 have been investigated. The use of the combined data from GC/FT-IR and GC/MS for sample analysis has also been demonstrated (6,7), and data obtained from directly linked GC/FT-IR/MS have been reported (8). These studies have demonstrated the need for vapor phase infrared spectral data bases that include PAHs containing four or higher aromatic rings (6). The use of GC/MS for identification of PAHs is a powerful technique for obtaining molecular structural information but most conventional electron impact ionization mass spectrometers (EI/MS) can lead to identical fragmentation of isomers and thus to identical mass spectra. Matrix isolation infrared spectrometry (MI-IR) has also been applied for PAH identification (9,10), in mixtures containing up to 5 components and gas chromatography matrix isolation (GC/MI-IR) spectra of several PAHs have been recorded (11). The quality of MI-IR spectra is dependent on the type of matrix used and the ratio of matrix to sample. Both these factors can cause infrared band splitting and band shifts and can change full width at half height (FWHH) of some bands.

In order to increase our capability for identification of PAHs and in order to distinguish between their many isomeric configurations we have measured the GC/FT-IR spectra of 33 PAHs and created a vapor phase infrared spectral library. These spectra reveal that the spectral region from 700 to 1000 cm^{-1} containing the aromatic C-H and -CH$_2$ out-of-plane and C-C in-plane bending modes can provide unique information for each isomeric compound.

EXPERIMENTAL

A. CHEMICALS.

Solutions of PAHs were prepared by dissolving 1-2 mg of each standard in 1 ml of toluene. Benzo[a]anthracene, benzo[b]anthracene (80% purity (UV)), benzo[a]fluorene (>98% (HPLC)), benzo[ghi]perylene, coronene (97% (HPLC)), 9,10-dimethyl anthracene (97% (HPLC)), dibenzo[a,c]anthracene (>97% (UV)), dibenzo[a,h]anthracene, 7,12-dimethylbenz[a]anthracene, 2-methyl anthracene (>99% (HPLC)), triphenylene (>98% (HPLC)) and Perylene (>99% (HPLC)) were purchased from Fluka AG, chem.Fabrik. Benzo[c]phenanthrene (Community Bureau of References), anthracene (Aldrich, 99.9%), benzo[a]pyrene (Aldrich, 98%), benzo[b]fluoranthene (Supleco, Inc.), and benzo[k]fluoranthene (Supleco, Inc. 99%) were also used for sample preparations. 9-Methyl anthracene, 3-methyl cholanththrene, O-terphenyl, M-terphenyl and P-terphenyl were obtained from Eastman Kodak Co. and acenaphthene, acenaphtylene, fluorene, fluoranthene, and phenanthrene were obtained from EPA Research Triangle Park.

B. INSTRUMENTATION

A Nicolet 5SX (Madison, WI) FT-IR spectrometer equipped with a 0.1 mm HgCdTe cryogenic detector and an air cooled nichrome wire source was used to measure the GC/FT-IR spectra. A Hewlett-Packard 5890 (Palo Alto, CA) gas chromatograph equipped with a splitless injector, a wide bore column (cross-linked methyl Silicon Gum, 25m x 0.32mm x 0.17 micrometer film thickness) and a flame ionization detector were used for the separation. The dimensions of the GC/FT-IR light pipe interface used were 12 cm x 0.1 cm. Using the above combination, interferograms were collected at a sampling rate of 50 kHz and an optical retardation of 0.125 cm. Either the Gram-Schmidt orthogonalization or the ChemiGram methods were used to reconstruct a real time chromatogram from the interferogram and the low resolution infrared spectra (12). At the end of the experiment the appropriate number of the interferograms were coadded and Fourier transformed to obtain the infrared spectrum of each compound.

For the preliminary analyses of PAHs the LSB routine method PAAPAH-AC8NCQ.21 (1) was used. This resulted in obtaining GC/FT-IR spectra of low signal-to-noise ratio (SNR). This method was modified in several ways to enhance the spectral SNR. A wide bore column was used to make an injection of a higher volume of the sample possible. We also employed on-column injection instead of split injection without masking the lower boiling PAHs (e.g. tetralin and naphthalene) under the solvent band and no make up gas was used to prevent analyate dilution in the light pipe.

The signal of the cryogenic Hg-Cd-Te detector decreases with increasing temperature of the light pipe. This phenomenon is attributed to (1) the temperature induced changes in the reflectivity of the gold coating inside the light pipe and (2) the masking of the modulated infrared signal from the interferometer by the unmodulated thermal radiation from the light pipe. For our detector, we observed a loss of about 45% of the signal by increasing the light-pipe temperature from 50 to 290°C. The boiling points of the PAHs can vary from approximately 200 to 600°C. Hence, the light pipe had to be operated at its optimum temperature which is about 285°C throughout our investigation. This represents a loss of about 45% of signal intensities in our experiments.

RESULTS

The sensitivity of the GC/FT-IR was first evaluated using the following experimental conditions. The light pipe temperature was set at 280°C, the column head pressure was varied from 5 to 20 psi and the GC/FT-IR spectra of a solution of dimethyl phtahlate (DMP) in toluene was recorded. For 60-nanogram DMP injected at a column head pressure of 15 psi, we could achieve a SNR of 10 for the most intense band in the spectrum. Lower detection limits have been reported in the literature, but the operating conditions have been very different in those studies. The light pipe temperature in those cases has been set between 170 to 240°C. From the relationship between the signal of the detector and the light pipe temperature it becomes clear that we will have a detection limit of 30 nanogram if we use a light pipe temperature of about 200°C.

In the preliminary work the vapor phase spectra of 10 PAHs were collected. These 10 PAHs are among the 13 PAHs for which vapor phase spectra exist in the EPA library. The temperature of the light pipe and the transfer line were set at 285°C, and the GC was temperature programmed from 80 to 300°C with an initial two minutes hold at 80°C. The GC oven temperature was ramped at a rate of 8 to 20°C/min, depending on the type of the sample, to 300°C. The quality of our spectra were either equivalent or in some instances, superior to those in the EPA library. Table 1 gives the list of these compounds (numbers 1 to 10). Under the same experimental conditions we obtained the GC/FT-IR spectra of the other PAHs (compounds number 11 to 33). The spectrum of each compound was measured at least three times to obtain the best quality possible. When necessary, solutions were concentrated by evaporating some of the solvent. Attempts to obtain the infrared spectra for Picene and Coronene were unsuccessful. Picene has a very low solubility in toluene or any other organic solvent at room temperature. Coronene has an estimated boiling point of about 590°C. Chrysene, Dibenzo[a,h]Anthracene, Perylene and Benzo[ghi]Perylene have relatively lower solubility than other PAHs in organic solvents which resulted in obtaining spectra with lower SNR.

These spectra have been transferred from the Nicolet 620 computer to the MS/DOS system in the Spectral Calc format, Thus forming part of the Ontario Ministry of the Environment vapor phase infrared spectral library of the PAH standards. This library will be expanded with other types of PAHs such as alkyl and halogen substituted, nitro-PAHs and heteroatom containing PAHs.

The creation of this library allowed us to attempt to identify the components of a mixture. The experimental condition were as before except for the use of a DB-5 25m x 0.33 i.d. x 1.0 micrometer film thickness capillary column. A sample of standard solution of PAHs mixture (3 microliters) was injected into the GC column and a GC/FT-IR analysis was carried out. Figure 1 shows the out put obtained from FID and the Gram-Schmidt reconstructed chromatograph for this analysis. After Fourier transformation of the interferograms the spectra were searched using the EPA library which has a total of 5010 entries. For those components whose infrared spectra are in the library , the correct identification was provided. For eight components for which there is no vapor phase spectra in the library, four best matches were given, all of which were incorrect. We were able, however, to identify correctly these PAHs using the newly created library. This experiment emphasizes the importance of creating an MOE library of PAH infrared spectra which enables the identification of the target PAHs encountered in the province of Ontario.

DISCUSSION AND CONCLUSION

Table 1 lists the PAHs investigated in the current study and the infrared absorption bands with significant intensities in the region 650 to 4000 cm^{-1}. Figure 2 shows the GC/FT-IR spectra of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]pyrene and perylene, five PAH isomers with five rings and molecular weight of 252.3, in the spectral region 650 to 4000 cm^{-1}. Several changes in the apperanece of infrared spectra, such as frequency shifts and changes in the relative intensities, are associated with changes in the physical state of a compound. For example, the infrared bands associated with the C-H aromatic stretching shift toward higher frequencies and those associated with C-H out-of plane bending modes often shift toward lower frequencies as the state of the matter changes from condensed to vapor state. Also, some active modes in the spectra of the condensed phase become inactive in the gas phase or show a considerable decrease in intensity. This is observed for the most of the vibrational modes associated with C-H in plane bending and CC stretching modes. The simplicity of the vapor phase spectra (see Figure 2) could be considered advantageous for fast identification of the components of a complex environmental sample mixture.

While we are in the process of accumulating more vapor phase infrared spectra to enhance our capability for identification of the PAHs, it is also recognized that due to the large variability cf PAHs which can be present in complex environmental sample mixtures other methods for fast identification must be explored. Program for the Analysis of InfraRed Spectra (PAIRS) which was originally developed by Woodruff and Smith (13), has been implemented recently in our laboratory on a 386 based personal computer running MS/DOS (14). The information flow in

PAIRS$^+$ is similar to the reasoning a chemist uses in interpreting spectral data. The computerized interpreter requires as input the spectrum, supplemental information and interpretation rules. As output, the program prints probabilities for each functional group under consideration. We have used PAIRS$^+$ to interpret the PAHs listed in Table 1 with different degrees of success. The result of analysis using PAIRS$^+$ to identify triphenylene is given as an example in Table 2. It is interesting to note that the strongest infrared absorption peak for triphenylene and for thiophene are positioned at 737 and 714 cm^{-1} respectively. Since PAIRS$^+$ interprets each spectrum based on peak locations, peak intensities, and peak widths, and since at this time we have not incorporated the interpretation tree for the PAHs the most probale functionality was interpreted as thiophene. The next two probablities i.e., aromatic and aromatic 1,2-substituted seem reasonable conclusion for triphenylene. At the time of writting this manuscript we are in the process of writting and testing an interpretation tree for PAHs in the vapor state. It is hoped that this interpretation tree for PAHs can make the "functional group frequency" screening of PAHs possible.

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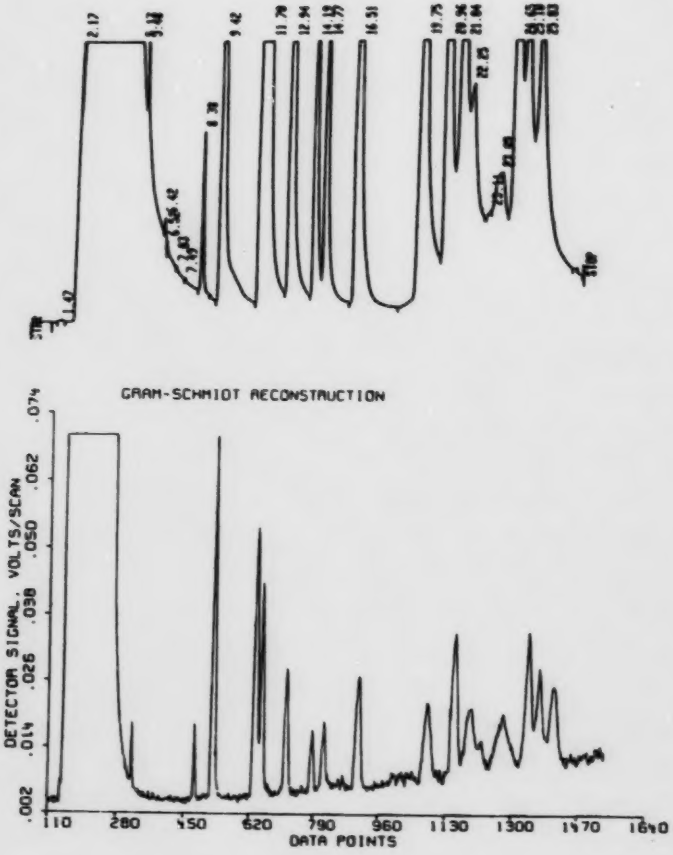

Figure 1- The gas chromatograph and the Gram-Schmidt reconstructed chromatograph from the analysis of a mixture of PAHs standard solution.

Table 1- The infrared absorption bands for PAHs in the spectral region 650 to 4000 cm-1 (The peak with the highest intensity in each spectrum is underlined).

1)Naphthalene	779, 1006, 1507, 3065
2)2-Chloronaphthalene	739, 806, 849, 880, 943, 1074 1137, 1192, 1232, 1345, 1454, 1593, 1628, 3066
3)Anthracene	724, 874, 1538, 3063
4)Phenanthrene	730, 806, 860, 1037, 1239, 1454 1500, 3065
5)2-Methyl anthracene	733, 1457, 1536, 1636, 2874, 2931 3057
6)9-Methyl anthracene	726, 773, 829, 996, 1306, 1346 1386, 1524, 1689, 2888, 3062, 3082
7)Fluorene	736, 1001, 1177, 1412, 1453, 1481 2916, 3028, 3071
8)Acenaphthylene	722, 770, 829, 859, 1084, 1148 1387, 1421, 1461, 1619, 1804, 1918 2946, 3063, 3100
9)Acenaphthene	782, 834, 1366, 1427, 1607, 2854 2898, 2940, 3054
10)O-Terphenyl	700, 748, 1009, 1067, 1437, 1473 1597, 3031, 3069
11)M-Terphenyl	699, 749, 796, 893, 1026, 1404 1447, 1474, 1497, 1594, 3036, 3069
12)P-Terphenyl	697, 751, 838, 1007, 1482, 1525 1598, 3034
13)1-Methyl phenanthrene	744, 799, 876, 1461, 1599, 2881 2938, 2978, 3064
14)Fluoranthene	741, 773, 825, 1426, 1454, 3066
15)Pyrene	708, 740, 837, 1182, 1432, 1596 1786, 3051
16)Benzo[a]fluorene	715, 753, 813, 1016, 1469, 2906 3066

...continued

Table 1 - Continued...

17)Benzo[b]fluorene	723, 766, 865, 953, 1017, 1188 1306, 1415, 1437, 1473, 1503, 2914 3024, 3064
18)Triphenylene	737, 1049, 1435, 1495, 3032, 3084
19)Chrysene	756, 807, 858, 1030, 1424,3066 3089
20)Benzo[a]anthracene	744, 799, 880, 1038, 1276, 1454 1500, 1681, 3062
21)Benzo[c]phenanthrene	667, 744, 795, 832, 863, 1030 1229, 1417, 1496, 3014, 3058
22)Benzo[b]fluoranthene	740, 774, 887, 1442, 1454, 1524 1599, 3071
23)Benzo[k]fluoranthene	740, 771, 821, 880, 1265, 1426 1446, 1611, 3063
24)Benzo[a]pyrene	687, 741, 757, 821, 845, 879 1023, 1079, 1185, 1263, 3057
25)Benzo[e]pyrene	744, 766, 826, 1440, 3056, 3086
26)Perylene	762, 812, 1383, 1589, 3059, 3087
27)Indeno[1,2,3cd]pyrene	730, 837, 879, 1381, 1443, 3057
28)Benzo[ghi]perylene	752, 768, 841, 3055
29)Dibenzo[a,c]anthracene	717, 755, 877, 1432, 1493, 1508 3066, 3077
30)Dibenzo[a,h]anthracene	739, 801, 881, 1023, 1088, 1454 3077
31)9,10-Dimethyl anthracene	743, 1367, 1389, 2941, 3088
32)7,12-Dimethyl benz[a]anthracene	745, 805, 2934, 3073
33)3-Methylcholanthrene	742, 799, 869, 1503, 2866, 2893 2929, 3049

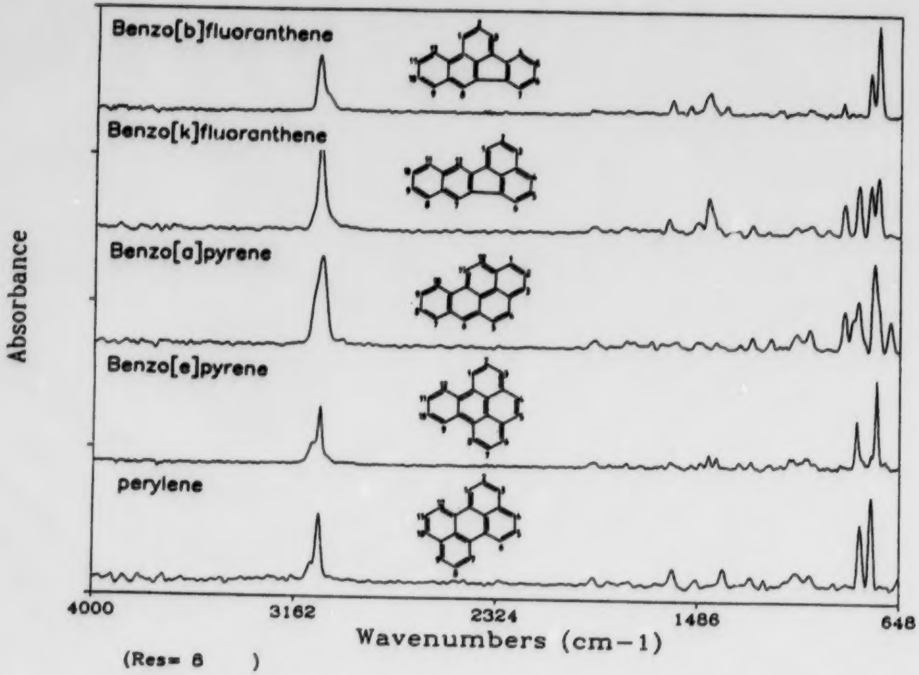

Figure 2- GC/FT-IR spectra for benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo [e]pyrene and perylene.

Table 2- The final report from PAIRS+ for triphenylene.

```
The final report from the upgraded PAIRS:


Spectral data summary for:

TRIPHENELYNE

The solvent is: neat

No empirical formula given

There are     6 peaks
Line   Width   Intensity   Location
   1   sharp         1         617
   2   average      10         737
   3   average       2        1435
   4   average       1        1496
   5   average       1        3032
   6   average       3        3086

==================================================
Printout is sorted by probability:

          Group name      Probability
  1)  THIOPHENE              0.60
  2)  AROMATIC               0.55
  3)  AROM-1.2-SUBST         0.55
  4)  OLEFIN-(NON-AROM)      0.20
  5)  OLEFIN-CH2=CR2         0.20
  6)  OLEFIN-CHR=CR2         0.15
  7)  OLEFIN-CHR=CHR(T)      0.15
  8)  OLEFIN-CHR=CHR(C)      0.15
  9)  OLEFIN-CHR=CH2         0.13
 10)  FURAN                  0.10
 11)  AROM-MONOSUBST         0.06
 12)  AROM-1.3-SUBST         0.06
 13)  HETEROAROMATIC         0.06
 14)  PYRIDYL                0.06
 15)  PYRAZYL                0.06
 16)  PYRIMIDYL              0.06
 17)  PURINE                 0.06
 18)  INDOLE                 0.06
 19)  PYRROLE                0.01
 20)  Z1                     0.01
```

D10

The Struggle Towards Virtual Elimination of Toxic Chemicals from the Environment

F.W. Karasek Award Address

D. Mackay
Department of Chemical Engineering and Applied Chemistry, and
Institute for Environmental Studies
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It is appears that we are in the midst of a profound change in society's attitude towards contamination of the environment by chemicals. There is a growing public intolerance of the presence of even very low concentrations of chemicals in air, water, food and wildlife. Degraded environments are viewed with increasing disgust and anger. The concern is particularly strong in the Great Lakes Basin where the concept of "virtually eliminating" toxic chemicals from the environment has been warmly embraced by a receptive public. But there is difficulty defining what this means, how it is to be accomplished, and especially what concentration goals it represents.

Environmental scientists and managers, in industry, government and the academic world, while attempting to respond to these demands are also experiencing difficulty coping with "explosions" in (i) analytical capability to detect miniscule quantities of chemicals, (ii) the number of environmental media which must now be analysed and assessed, (iii) the number of candidate chemicals of concern, (iv) data on these chemicals' subtle toxicology and (v) in regulations pertaining to chemical use exposure and discharges.

Environmental science technology and regulation are lagging behind public and hence political demands, forcing decisions to be made in the absence of adequate knowledge. There is thus a compelling incentive to undertake more well-directed research in the hope that it will lead us to a better understanding of the sources, fate and effects of chemicals in the environment, and to effective and economic controls which will satisfy the public's increasing demands.

Although much remains to be done we should acknowledge that the 1970s and 1980s have seen the emergence of a formidable body of knowledge concerning the number and nature of chemical contaminants, and their physical-chemical, biological and toxicological properties. We have a remarkable, and still increasing, capability of detecting the presence of chemicals at very low concentrations in all compartments of our ecosystem. We now know that chemicals behave in a generally predictable way, migrating throughout the various media of the environment, and often concentrating to remarkably high levels in particular locations such as animal lipids and aerosols. It should now be possible to avoid repeating past mistakes such as the excessive releases of DDT, PCBs and mercury. To guarantee this we need an improved capability of assessing environmental fate and toxicity of chemicals.

A system appears to be evolving in which certain chemicals such as PCBs will be totally banned from commerce; others such as lead or mercury will be used, but in limited quantities and under strictly controlled conditions of compulsory recycle or disposal; and the remaining relatively benign chemicals which remain in general use will be discharged to the environment only in known, small, acceptable quantities after state-of-the-art or "best available" treatment and with a full assurance that their fate and effects are well understood. It will be no longer acceptable to discharge chemicals indiscriminately, surreptitiously, or in large quantities, especially when there is suspicion of any effect on ecosystems or on human health. A view is emerging that the best guarantee of human health is not to shield ourselves from contamination but to work towards creating a healthy contaminant-free ecosystem in which the most sensitive wildlife species thrive. Essentially, society will manage all chemicals from cradle to grave with special attention to those which are most toxic and persistent.

It is suggested that the current of changing public attitude of demands for a high quality ecosystem, and assurance of unimpaired human health is taking us in this direction. Assurances that chemical concentrations and exposures are low and will probably not produce adverse effects are increasingly falling on deaf, unreceptive ears. There is a growing demand for simple elimination of chemicals from the outdoor and indoor environments, and the workplace, regardless of the chemicals' nature, concentration or toxicity. This creates a considerable challenge for the community of environmental scientists and managers whose task it is to respond to these demands with a full awareness of the current state of the art, economically, professionally and with sensitivity.

D11

GRAPHICAL TECHNIQUES FOR THE PRESENTATION OF INTERLABORATORY STUDY DATA - A DIAGNOSTIC AID

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ABSTRACT

Historically, most interlaboratory studies have documented current performance and evaluated the performance against a standard in tabular form. Graphical techniques of evaluation provide for a more immediate comparison of performance and a greater incentive for participants to improve their performance. Examples from a series of interlaboratory studies co-ordinated by Laboratory Services Branch of Environment Ontario during 1988-90 demonstrated this approach.

INTRODUCTION

The role of the interlaboratory or collaborative study to establish the precision of an analytical procedure is well established. The American Society for Testing and Materials (ASTM) and the Association of Official Analytical Chemists (AOAC) have published guidelines for conducting this type of study (1, 2). The data is treated and summarized using classical statistical techniques and an accepted standard of performance is established.

Interlaboratory performance studies are then used as a means of monitoring the ongoing performance of a group of analytical laboratories that are testing environmental samples. These studies have three functions: documentation of current performance, evaluation of that performance against a standard, and inducement to improve both individual and group laboratory performance

(3). There are many examples in the literature of interlaboratory performance studies that tabulate current performance and evaluate the performance against a standard using classical statistical techniques. Less frequently are the interlaboratory studies used to focus on ways to improve an individual laboratory's performance.

MOE LABORATORY SERVICES BRANCH APPROACH

The Laboratory Services Branch (LSB) of Environment Ontario initiated a series of Interlaboratory Performance Management Studies in 1988 in support of the ministry's Municipal and Industrial Strategy for Abatement (MISA) Program. The studies were designed not only to document the current level of performance of laboratories capable of performing MISA analyses, but also to be used as a tool for improving an individual laboratory's performance. Each study focused on a specific MISA analytical test group or groups (4), with different tests being repeated over time so as to monitor improvements in performance.

The traditional approach of reporting interlaboratory means, medians, and standard deviations for the various parameters has been included for the LSB studies, as they provide a familiar form of comparison for the participants. However the assessment of each individual laboratory's performance, and the recommendations for improvement are based on different graphical techniques.

The Youden two-sample plot (2) is a well-established technique for assessing intralaboratory precision. Traditionally it has been applied to single-parameter tests. The standard deviation of the results can be used to calculate a limit for acceptable performance, with outlying laboratories flagged (Figure 1). This approach works effectively for most conventional and inorganic analyses.

By applying the Youden two sample technique to the results from an organic gas chromatographic (GC) scan, the interanalyte repeatability and bias may be assessed for an individual laboratory (Figure 3). Tolerance limits may be assigned or calculated, to rank the precision and the bias of the data set. Outlying parameters may be flagged, as opposed to flagging an outlying laboratory.

To assess a laboratory's performance across a GC scan, the results from a sample may be converted to percent recovery of the design value, arranged in elution order, and presented as a bar graph (Figure 5). Trends across the scan may be noted, with recommendations for improvement. This may include patterns of increasing or decreasing recovery, suggesting adjustments for the GC temperature programming. A specific group of parameters within the scan may be over- or under-recovered, suggesting problems with extraction efficiency. Individual problem parameters are easily identified, and steps can be taken to check calibration standards or the appropriateness of the method for a specific parameter.

The following examples from several different LSB Interlaboratory Studies demonstrate how these graphical techniques may be used as a diagnostic aid to help improve laboratory performance.

EXAMPLES

Interlaboratory Study 89-6: Metals and Hydrides

Interlaboratory Study 89-6 was conducted in September 1989 to assess the interlaboratory variability for the analysis of metals and hydrides in spiked reagent water. A total of 36 laboratories participated in this study (5).

The traditional Youden two-sample plot was used to assess the results from this study (Figures 1 and 2). To evaluate the results and determine outliers, a pooled standard deviation of the two spiked samples was calculated (5). This acceptance criteria is indicated by the circle on each plot and outlying laboratories are flagged. The location of the outlying results in either the upper right or lower left quadrants, demonstrates either a systemic high or low bias, usually associated with a difference in calibration standards.

Interlaboratory Study 89-5: Acid and Base/Neutral Extractables

Interlaboratory Study 89-5 was conducted in May 1989 to assess the interlaboratory variability for the analysis of acid and base/neutral extractables in spiked reagent water. A total of 15 laboratories participated in this study (6).

The Youden two-sample technique was applied to the results across the GC scan after converting the results to percent recovery of the design value. Tolerance limits of ±20% for performance were assigned (Figures 3 and 4). Interanalyte repeatability can be deemed acceptable if all the data pairs fall within the tolerance limits, as demonstrated in Figure 3. Biases within the scan can be easily recognized as demonstrated in Figure 4.

Interlaboratory Study 89-1: Volatile Organics

Interlaboratory Study 89-1 was conducted in January 1989 to assess the interlaboratory variability for the analysis of volatile organics in spiked reagent water. A total of 16 laboratories participated in this study (7).

To assess the performance across the GC scan, the results were converted to percent recovery of the design value, arranged in approximate order of elution, and plotted as a bar graph (Figure 5). The results demonstrate various patterns of performance. Laboratory 1007 demonstrates a pattern of increasing recovery across the scan, suggesting that the temperature program may initially be too high, resulting in volatilization of the target parameters. Parameters that are over-recovered are readily identified, suggesting that the calibration standard should be cross-checked for accuracy. The results for Laboratory 1014 indicate a subset of parameters that demonstrate a pattern of decreasing recovery across the scan. This may indicate that the method used by this laboratory is not appropriate for the analysis of these parameters.

CONCLUSION

Graphical presentation of interlaboratory data can facilitate interpretation, and reveal patterns that are not detected by tabular or statistical summaries. They provide a fresh perspective and insights into relationships which may otherwise be overlooked or missed, providing greater incentive to improve laboratory performance.

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6. *Interlaboratory Study 89-5: Extractable Organic Parameters in Reagent Water*. 1990. Draft.

7. *Interlaboratory Study 89-1: Volatile Organic Parameters in Reagent Water and Oil and Grease in Reagent Water and Effluent*. July 1990. Queen's Printer for Ontario. ISBN 0-7729-7164-1.

FIGURE 1

FIGURE 2 :INTERLABORATORY STUDY 89-6

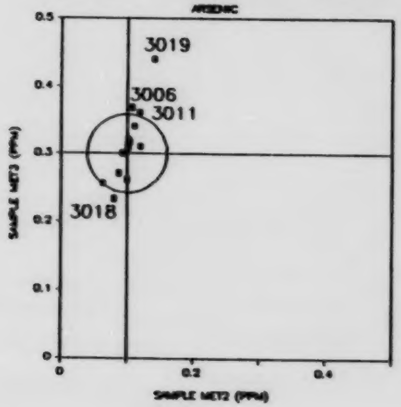


FIGURE 2

FIGURE 12:NTERLABORATORY STUDY 89-6

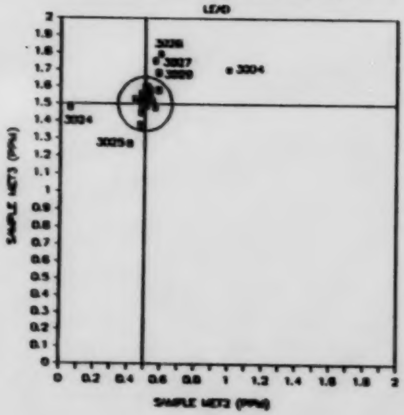
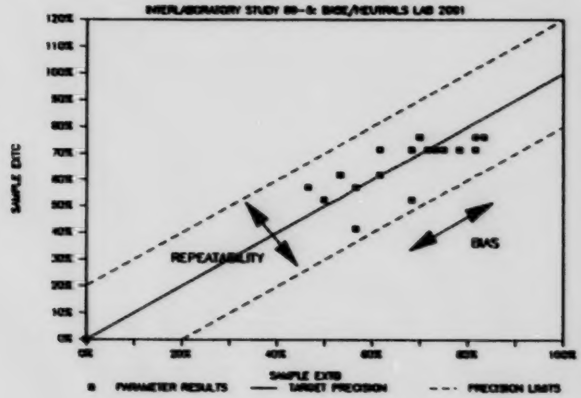


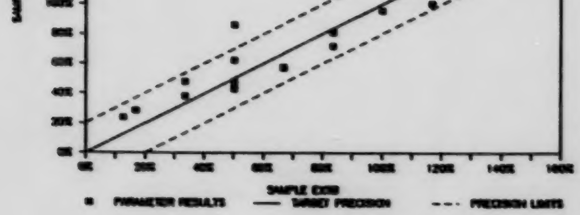
FIGURE 3



INTERANALYTE BIASES

INTERLABORATORY STUDY 88-5: BASE/NEUTRALS LAB 2001

FIGURE 4



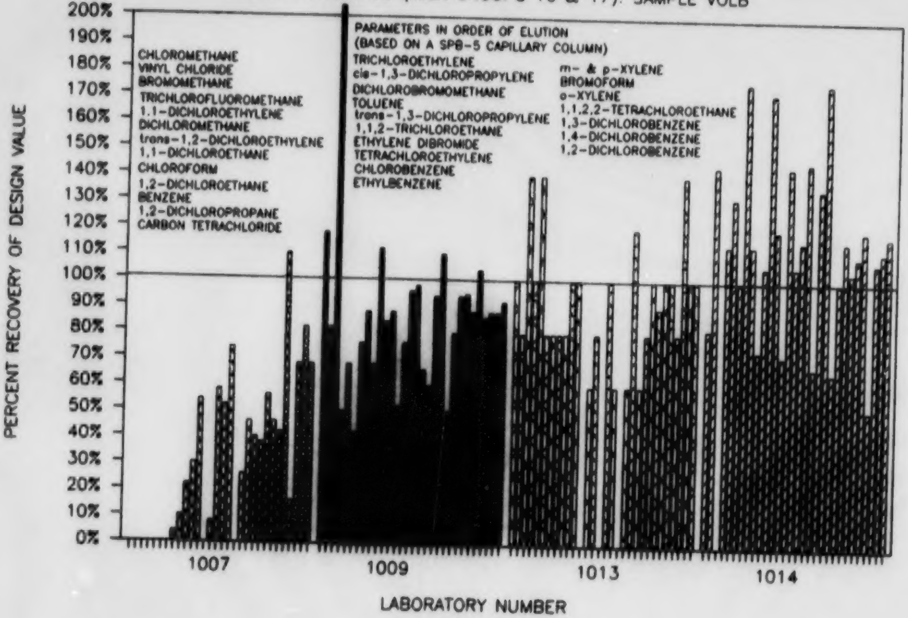
INTERANALYTE BIASES

INTERLABORATORY STUDY 88-5: ACIDS LAB 2011

FIGURE 5

FIG. 3 – INTERLABORATORY STUDY 89-1

VOLATILE ORGANICS (MISA GROUPS 16 & 17): SAMPLE VOLB



D12

Design, Constraints and Implementation of Rules Within ACexpert.

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London, Ontario, CANADA, N6A 5B7

Abstract The full value of expert systems in solving analytical chemistry problems can only be realized when the technical methods used to create these complicated programs are understood by analytical chemists. While the knowledge base, inference engine and user interface needed in each expert system can be written in either a procedural language (such as C or FORTRAN), or in a specially developed language like LISP or Prolog, the expert system shell appears at this time to offer the most reliable and productive route for the analytical chemist to follow. Expert system shells provide a programming environment that primarily offers built in subsystems that can acquire facts and rules and operate the inference engine. In this paper, we describe the continuing development of the expert system, **ACexpert**, a program which will control all aspects of metal ion determination carried out by atomic absorption spectrometry. Our present work involves coding analytical method and diagnostic rules for use with the analytical methods selection module **ACmethods** and the quality control module **ACdiagnostic**.

Introduction

Expert system programs offer the analytical chemist several distinct tools for use in the laboratory. At the present time, it is possible that their most important value is in providing rapid access to chemical information that has been verified for highly specific tasks, and that is presented to the user in a highly organized manner. This view of the role of an expert system readily leads to the use of expert system programs as advisors for methods development and for analytical problem solving. Prior to the introduction of expert system shells, the development of expert system software required a considerable investment in both money and time. With the advent of the expert system shell, the knowledge engineer, expert, and programmer may be one and the same person. As the capabilities of these expert system shells become better known to analytical chemists, we expect that these software packages will become as important as the procedural programming languages of FORTRAN, BASIC, Pascal, and C are today. Excellent examples of the application of expert system techniques within analytical chemistry may be found in two books edited by Pierce and Hohne[1,2], and we have discussed the results of earlier work on ACexpert previously[3-6].

Analytical chemists can use the expert system's capability to manipulate symbolic data to carry out many of the tasks currently completed with procedural programs, however, now the program can be coded to check that the results obtained by the calculation are reasonable. This type of program can be designed to operate instruments, which may be considered to be a 'black box' by their operators, 'intelligently'. We have considered[3,4] that instruments that fall under this class are atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), high performance liquid chromatography (HPLC), and gas chromatography-mass spectroscopy (GC-MS).

ACexpert has been designed to carry out completely automated metal concentration determination by atomic absorption spectrometry. Solutions of samples, blanks, modifiers and standards will be prepared by an automated liquid sample handling station, and then pumped into the flame of an atomic absorption spectrometer. This environment is well suited to test rule-based methods selection and quality assurance modules, as well as the incorporation of modules to access analytical information stored on different databases. Overall, **ACexpert** will act as an advisor and assistant to the analytical chemist in completing analyses.

Expert systems applications within the field of analytical chemistry[1-11] fall into two broad categories: (i) systems that are developed to interpret experimental results, and (ii) systems that provide guidance as to the course of action the analyst should take. The challenge in the development of an expert system is to produce a system that will dispense chemical advice at or near the level of a skilled chemist, while at the same time being capable of recognizing that both the skilled chemist and the computer expert system may at times make mistakes. The development of an expert system, must start with some concept of what an "expert" is, how experts perform scientific tasks, and how scientific "expertise" is acquired. There are two main characteristics that distinguish experts from novices. (i) Experts are usually expert only with respect to a narrow area of expertise, and (ii) they rely on shortcuts that they have distilled from their previous experience[12]. As a consequence, experts tend to rely more on pattern recognition and memory at the expense of deductive reasoning, than do novices[12,13]. We have found during our work that a major limitation in the use of a rule-based program is the complexity of the user interface. We find that expert users of the system are more comfortable when the questions and solutions are offered in a style that is equivalent to their knowledge in the field. This means that the user interface must allow information transfer between the expert and program to be as efficient as possible. In order to meet this challenge we are currently exploring the possibility of using Windows 3.0 (Microsoft) as well as using graphical images in place of textual statements of chemical or analytical status.

Structure of an Expert System

Expert systems consist of three important modular components: the user interface, the inference structure, and the domain knowledge or expertise, as shown in Figure 1. The arrows represent the formal exchange of information between each of these distinct subsections of the expert system. With the appropriate shell, the analytical chemist can customize these subsections to produce an expert system that will provide a new generation of programming assistance for solving chemical problems.

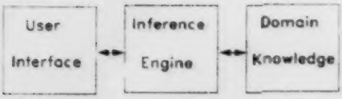


Figure 1. The Structure of an Expert System. The double headed arrows illustrate how information is exchanged between the three different modules of the program. It is important to the implementation of an expert system that there are no direct links between the user interface and the knowledge base. This allows the knowledge base to be changed after the program has been written.

Development environments for expert systems are known as shells. These shells are expert systems that generally contain an inference engine, and various interface and knowledge acquisition aids, but lack rules and facts in the knowledge base. We illustrate the structure of an expert system shell and its components in Figure 2. The use of these shells greatly simplifies the development of an expert system.

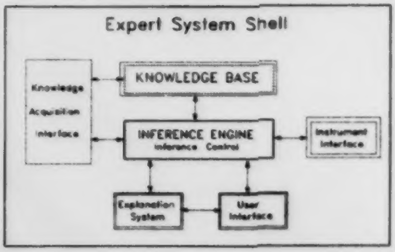
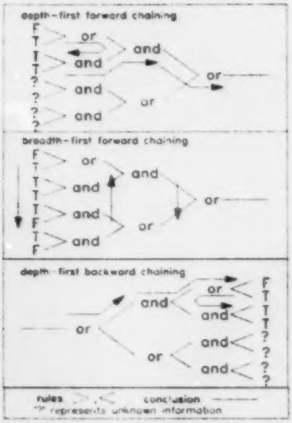


Figure 2. Structure of an Expert System Shell. Compared with an expert system language, the expert system shell includes an empty, 'shell', knowledge base and a knowledge acquisition module. In most simple expert systems the possibilities for modification of the explanation system and the user interface are limited. However, specialized interfaces such as an instrument interface can be added.

Inference engine The inference process involves asserting the conditions under which facts are true for certain knowledge or likely to be true for uncertain knowledge. Three inference strategies are commonly used: forward-chaining, backward-chaining, and the rule-valued method[12]. These inference strategies can be combined with either a depth-first or a breadth-first search strategy[12]. The depth-first search strategy, Figure 3, requires an affirmative search through all levels of a branch of the tree, until a contradiction or conclusion is reached. The breadth-first search strategy requires that each level of all the branches be searched before a conclusion is reached. In forward-chaining, the inference engine uses the user's information to move upwards through a tree of rules towards a single conclusion. In backward-chaining, the system starts with a conclusion (this could be an analytical method) and requests from the user data to confirm or contradict this conclusion (these data could be the matrix, element, solvent, concentration range, regulatory agency, etc.).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rules >, <
conclusion ——
"?" represents unknown information

Figure 3. Different logic strategies used by inference engines: Forward Chaining with a Breadth-First Search, Forward Chaining with a Depth-First Search, and Backward Chaining with a Depth-First Search. The arrows indicate a search path that may be followed through the tree of rules and clauses to arrive at a conclusion.

Knowledge base The knowledge base holds information in terms of data, as well as rules that link these data together. The information may be stored in the program itself or the knowledge base may be stored as a separate database. The developer's job is to acquire the necessary information for the knowledge base. This information will be a combination of personal experience of experts as well as published data.

Interface One of the most important aspects of the expert system is the implementation of the user interface. A good match between the system and the user is vital. The user interface has to handle all communication between the user and the expert system in a way that maximizes the flow of information. The expert system must be able to explain the reasoning behind its conclusions. An explanation subsystem is usually set up for this purpose. The knowledge engineer can also use this system to elaborate on the advice that is given to the user. Often, however, the explanation displayed simply takes the form of an exact textual copy of the rules that were used to provide the advice, so may not be at all helpful to anyone but another expert and certainly of no use to the novice user.

Comparison between Conventional and Expert System Programming

In the expert system, the separation of the knowledge base from the inference engine and the user interface, allows for modular expansion and easy maintenance of the knowledge base. In conventional procedural programs, the domain knowledge of facts and rules is completely integrated into the inference structure. This means that the developer must classify all of the objects and define all of the relationships and concepts that are to be used in the program before any code is written. Procedures are then created that will infer new instances of relationships from existing ones, in a sequential fashion. Like the execution of the program, the program is developed in a sequential fashion. The result of this integration is unwieldy development and practical limitations to the complexity and size of the system that can be produced.

By way of contrast, the development of an expert system is more circular and evolutionary. Often the detailed specifications of the program, and what it is to accomplish, are not well defined in advance. The relationships and concepts that are required to complete the logic of the expert system are discovered by the knowledge engineer and the expert during the development of the system prototype. In addition, expert system techniques typically attempt to separate the control structure from the domain knowledge. During the prototype stage of development, rules in the knowledge base may be easily changed or added in order to fine tune the reasoning.

One of the overwhelming features of chemical knowledge is that information, procedures, and techniques are always evolving. The amount and complexity of that knowledge is always increasing. The structure of a conventional programming environment, although efficient for repetitious rigidly defined tasks, is incompatible with the dynamic nature of developing chemical knowledge and systems that dispense advice. Expert system shells, which provide the chemist with a complete programming environment, relieve the expert of the task of creating the user environment. The chemist can focus on the problem at hand which is be the incorporation of his or her expertise into a program that will dispense advice by tailoring the shell to produce the working expert system.

ACexpert

Metal concentration determination using AAS requires the completion of several tasks, each of which require extensive knowledge and expertise. With the increased automation of modern instrumentation and the demands for increased efficiency and volume of analyses, the organization, operation and control of these complex tasks are well suited to the use of an expert system. Although the decisions about chemical analyses are complex, the procedures and methodologies of analytical expertise are well understood. For this problem the three most important criteria for the successful development of an expert system are fulfilled: (i) this is a significant problem for which there is a demand for a solution, (ii) acceptable expert system development tools are available, and (iii) the expertise which will be used to create the expert system is readily available from a variety of sources.

In an analytical laboratory, there are several steps that always take place between receipt of a sample and dispatch of the report. Typically, the manager consults with both the customer and the regulatory agency to determine the method that is to be used. The quality control and quality assurance programs and the report writing are carried out as separate tasks by the manager and the analyst. In terms of analysis by AAS, sample preparation is followed by determination of the concentration of metal by empirical comparison with a calibration curve for that analyte. QA/QC programs check the precision, accuracy and stability of the instrument over both the short and long term. Matrix effects, physical interferences, and spectral interferences are among the analyst's expert knowledge. Although incorporation of an expert system into the analytical laboratory will change how some of these tasks are carried out, the judgement and expertise of an analytical chemist or a skilled technician will still be needed to interpret the information offered by the computer system. We list in Table 1 specifications that we believe are necessary for an expert system that operates in an advisory or consultative role (see Table 2) within an analytical chemistry laboratory.

There are four steps tmust be completed in the development of an expert system program:

- (i) Problem determination and specification stage.
- (ii) Development of the initial demonstration prototype.
- (iii) Development of the expanded prototype.
- (iv) Completion of the deliverable system.

In our work to date, we have completed (i)[3-6], and are completing (ii), while exploring the technical difficulties involved in scaling up to (iii).

The problem determination and specification stage, requires the completion of a detailed description of the concepts, and the identification of criteria and case studies that will be used to produce a small version of the expert system in order to demonstrate its overall feasibility.

Table 1. Specifications for an expert system in an advisory role.

1.	the system should be built around a powerful user interface
2.	the system should be able to use the user interface to determine the conditions to be satisfied in an order of priority (analyte, regulatory body, analytical technique, sample type, etc.), and allow the user to determine the effect of a specific choice on the advice provided by the system.
3.	the system should have the ability to use generic rules that govern the measurement of analytical data as well as using specific methods stored on a database.
4.	the system should be able to use ambiguous information and also be able to offer multiple answers with some form of ranking, when necessary.
5.	the system should be able to access information stored by traditional database and spreadsheet programs.
6.	the system should be able to explain the reason for using the procedures suggested.
7.	the system should be able to integrate its decision making with other expert systems.

ACexpert encompasses the complete system that will be used to carry out completely automated metal concentration determination. The structure is described as a set of expert systems shown in Figure 4. Each expert system will perform a separate task and each will be capable of acting independently or as a module of the full system. In this scheme, the analyst's role fundamentally changes from one of a technician to that of a supervisor of the expert system, **ACanalyst**. However, the manager's role remains the same, although he or she now has the assistance of both the analyst and **ACexpert** in order to monitor the completion of analyses. **ACassurance** is the quality assurance expert system that will be used by the manager and the analyst to assist in the execution of a laboratory quality assurance program. Incorporated in this expert system are modules that will be used to provide instruction and advice to the laboratory personnel in carrying out their tasks and completing the analysis procedures thoroughly. **ACanalyst**, the quality control and process control expert system, comprises five separate expert systems that will be used in methods selection, process control, analysis, fault diagnosis, and quality control. The functions of the individual expert systems have been outlined previously[3-6].

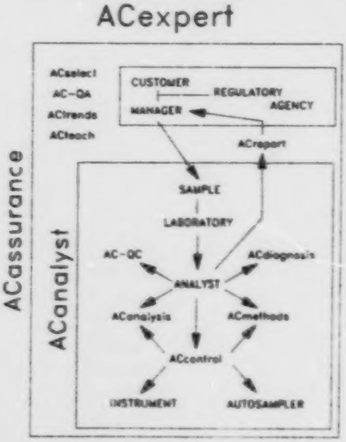
ACexpert
ACselect
AC-QA
ACtrends
ACteach
CUSTOMER
REGULATORY AGENCY
MANAGER
ACreport
ACassurance
ACanalyst
SAMPLE
LABORATORY
AC-QC
ACdiagnosis
ANALYST
ACanalysis
ACmethods
ACcontrol
INSTRUMENT
AUTOSAMPLER

Figure 4. **ACexpert** is a chemical analysis expert system which provides interactive assistance to the analyst. The flow of information or the movement of the sample is illustrated by the connecting lines.

In normal operation, the analyst would manually confirm the method selected by **ACmethods** and monitor the performance of the analyses. All other aspects of the analysis would be carried out automatically, although still under the direct supervision of the analyst.

The implementation of a demonstration prototype of each of the separate expert system applications is next step. Each task that the expert system is expected to complete may require a separate inference and knowledge base structure. The specifications for these structures may vary considerably depending on the task that it is to perform. For example, the structure of a consultative expert, will differ considerably from that of a real-time monitoring and control expert or an interpretive expert system. A summary of the types of expert systems, which might be useful to the analytical chemist is provided in Table 2.

At a minimum, a shell must have a knowledge representation scheme, an inference or search mechanism, a means of describing the problem, and a way to determine the status of a problem while it is being solved. Consultative or diagnosis experts, may be used for methods selection or fault finding (**ACmethods**, **ACdiagnosis**), and typically are built with rule-based shells that require consistent relationships between causes and symptoms, or conditions and conclusions, as well as the ability to identify these relationships. The decision making is made more difficult if symptoms are masked by other symptoms, the symptoms are intermittent, the data is inaccessible, or if there is uncertainty and lack of knowledge about the relationships between the causes and symptoms.

Table 2. Descriptions of specific types of expert system and examples of their use in the analytical laboratory.[8]

Type	Use
Consultation	Selecting a method from a list of ingredients or procedures; **ACmethods**, **ACtrends**
Control	Directing the overall operation of an instrument or process control system; **ACcontrol**
Diagnosis	Determining probable causes of malfunctions or incorrect data values from observables; **ACdiagnosis**
Instruction	Training operators and technicians through simulations and question and answer sessions; **ACteach**
Prediction and simulation	Inferring probable consequences from a given situation; **ACteach**, **ACanalysis**, **ACtrends**

Use of the KDS3 Expert System Shell

The KDS environment for expert system development, provides the developer with substantially the same interface and performance characteristics as the end product that the user will encounter. This shell, like many other inductive shells, generates rules from examples. The developer enters a large number of examples for the machine's information base into the development system. The development system then uses an algorithm to convert the examples into a rule or number of rules and to determine the order that the system will follow when questioning the user and making a recommendation. Unlike other production, rule-based systems, KDS does not deal with attributes or values, but only with conditions, which are input into KDS as text strings that are either true, false, or known with some degree of certainty[13]. To KDS, every entry is simply a string of text that has some factors associated with it and a certain place in the logical hierarchy (see the paper in this volume by S. Lahiri, Q. Zhu and M. J. Stillman, that describes in more detail the relationship between conditions and conclusions).

The KDS compiled expert system uses the knowledge of the conditions and rules that make up the knowledge base to ask questions of the user in the most efficient manner according to the number of times a condition has been used to arrive at a conclusion. For example, the KDS system will request validation of a condition that has been used by 4 conclusions before a condition that has been used by only 2 conclusions. However, as a consequence of the KDS inference strategy, which selects the ordering of the question, the questions may be asked in an unusual order for someone who is expecting a hierarchy relationship between the questions. For example, when the system begins to determine the information summarized in Table 3, the questions asked may not follow the route that we have used. Instead conditions that might be considered out-of-order are asked first.

The KDS expert system shell carries out its own testing and validation of the logic provided by first the developer, and then the user. During development, the KDS shell ensures that the logic connecting conditions does not change as more information is encoded; during use, the shell checks that answers provided by the user do not conflict with the logic originally given by the developer.

An inductive shell, such as KDS, provides an excellent prototype environment that has extensive interfacing capability to other systems and procedural programs in order to input information through a variety of special interfaces. The rigorous logic, which the developer must follow in order to create a usable expert system, results in well implemented system that can be used as a learning experience for the developer as well as the user. As indicated in the section on Experts and Expertise, it is often difficult for experts to report how a solution was arrived at. The "step by step", example-driven programming of an inductive shell, like KDS, provides an excellent environment for resolving the ambiguity of unclear rationalizations.

The **ACmethods** is based on data given in the Varian Canada applications manual for metal determination in aqueous samples. The prototype advice is presented to the user as simple text. As the expert system evolves, we will tailor the **ACmethods** manual to the needs of the local laboratory by incorporating access to methods stored as entries in a database. The first prototype of **ACmethods** uses a small set of attributes or conditions (analyte, regulatory body, analytical technique, sample type, sample preparation method, or detection limit) to determine the method to suggest to the user. As the **ACmethods** expert system grows in complexity this set of attributes will need to be expanded.

Implementation of ACmethods

The knowledge base for **ACmethods** was implemented with the KDS3 development system.

Table 3. User-provided information to be transferred from the user interface to **ACmethods** in order for a method to be selected.

	Control information for **ACmethods**	Choices available
1.	Analytical technique to be used	Atomic absorption spectrometry.. flame, vapour phase, graphite furnace (AAS) Inductively-coupled plasma atomic emission spectrometry (ICP-AES) gas chromatography (GC) liquid chromatography (LC) ion chromatography (IC) GC-MS
2.	Element to be analyzed for	Periodic Table appropriate for technique
3.	Known interfering elements	Periodic Table or Dictionary appropriate for technique
4.	Matrix for sample	Natural waters Sediments Organic material Effluent
5.	Chemical properties of the analyte	Mineral acid-extractable metal Metal in suspended material of sample Metal can be extracted with organic solvent to eliminate interferences
6.	Regulatory agency	Ministry of the Environment, Ontario Water Quality Branch of Environment Canada in Ottawa

In this example, the expert system presents the user with both menus and individual questions during the course of the session in order to select the appropriate method. In a more complex expert system the KDS standard interface could have been replaced with a customized user interface or an instrument interface, if real-time data input and analysis were desired.

Discussion

Success in the development of a new expert system is strongly dependent on the planning stages which must include a significant component of system validation and evolution. The challenge for the chemist will be to become knowledgeable about the available expert system shells that can be used in the development of prototypes. As the degree of complexity increases, so the developer will have to begin to use tools that are more sophisticated in order to handle decision making. These tools will include frames, objects, and blackboards. However, like any programming environment, shells that incorporate the more sophisticated knowledge representation strategies will make greater demands on the programming skills of the knowledge engineer.

Several modules in **ACexpert**, such as **ACmethods, ACselect, ACtrends,** and **ACteach,** will require extensive access to a database in order to supplement the complex rules and facts that will be needed to provide advice from more involved or ambiguous information. For such systems an expert system shell that organizes knowledge as objects or in frames will be required.

Acknowledgments

We wish to acknowledge the significant work that Dr. William Browett carried out on the initial stages of this project and we wish to thank the Ontario Ministry of the Environment, NSERC and the Academic Development Fund at the UWO for continuing financial support.

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Glossary

Backward Chaining: An inference control strategy that regulates the order in which inferences are drawn. In a rule-based system, backward chaining is initiated by a goal. The system attempts to prove the specified goal by determining the truth of the clauses that become secondary goals.

Breadth-first Searching: A search strategy in which all rules at the same level of a particular hierarchy are pursued before moving to the next level.

Conventional (procedural) language: A language in which an algorithm for solving a problem is expressed in an objective form and can be used repeatedly to solve a variety of problems that can be addressed by the same algorithm.

Depth-first Search: A search strategy in which all levels of a specific conclusion are pursued as deeply as possible until that conclusion is proven true or false. The system searches down a single branch of a tree until it reaches the end. It then backs up to the first unsearched branch and goes down that branch, and so on.

Domain: A subject matter area or problem-solving task.

Expertise: Skill, knowledge, rules, and procedures in a particular domain. These characteristics imply not only knowledge of the domain, but also the ability to organize this knowledge into chunks and networks for practical use.

Expert system shell: A very high-level expert system language that permits the construction of very powerful systems with a minimum of programming.

Explanation System: That part of an expert system that permits the user to query about the reasoning process used in reaching a particular goal state.

Forward-chaining: A type of reasoning strategy that begins with the known facts and works forward, trying to find a goal for which all of the facts are true.

Frame representation: A type of knowledge representation in which an object is associated with a number of attributes or properties, and the attributes are associated with values. The object is represented by a frame, the attributes by slots in the frame, and the values are stored in the slots.

Hierarchy: An ordered network in which some objects are subordinate to others. Hierarchies imply inheritance. Objects at the higher level are the parent, and objects immediately subordinate are the children.

Induction system: (or Example-driven system) A knowledge system that generates a decision tree or rules from a set of examples.

Inference engine: That part of an expert system that infers new facts from existing facts using rules in the knowledge base, and also control the order of inference.

Knowledge: Facts and relationships about a particular domain that can be used to solve problems in that domain.

Knowledge base: A knowledge base is a database that is constructed by the knowledge engineer and an expert to hold specific information and rules about a certain domain.

Rule-based system: A type of knowledge representation in which knowledge about a domain is expressed in rules that describe relationships between.

AN APPARATUS FOR RAPID MICROWAVE SAMPLE DECOMPOSITION

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A. Introduction

There is little doubt that the speed of analysis offered by many modern elemental analysis instrumentation systems is orders of magnitude faster than traditional (i.e., open-vessel, hot plate) sample digestion procedures. Therefore, digestion methodologies and instrumentation that offer high throughput are of paramount importance, especially for laboratories that must handle large numbers of samples.

The goal of this work is the development of rapid (i.e., less that 5 min) stopped-flow digestion instrumentation and methodology for botanical and biological samples of interest to the Ontario Ministry of the Environment (MOE). As in our earlier work [1, 2], a Teflon tube serves both as a sample container and as a digestion vessel. Besides the advantages mentioned above, the closed vessel, elevated temperature and pressure approach used here minimizes the risks of sample cross contamination when digesting multiple samples simultaneously and of acid fumes attacking the oven components. It also offers additional safety protection to personnel by limiting exposure to hazardous acid fumes and by minimizing reagent handling. Ease of automation is, perhaps, the most important advantage of this approach.

B. Instrumentation

A block diagram of the instrumentation developed in this work is shown in Fig. 1. The system consists of a peristaltic pump, two high pressure valves, a microwave oven, a "tube assembly", a pressure gauge and a temperature transducer.

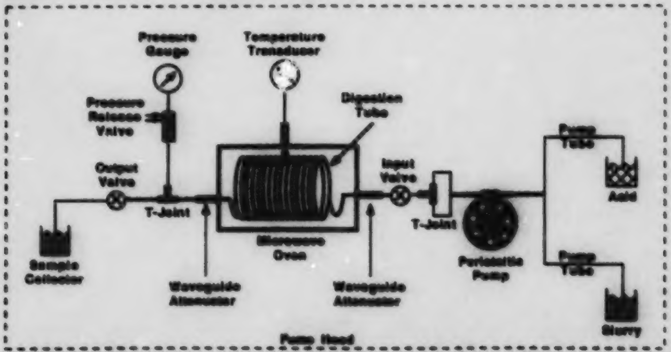
Pressure Gauge
Temperature Transducer
Pressure Release Valve
Digestion Tube
Pump Tube
Output Valve
Input Valve
Acid
T-Joint
T-Joint
Microwave Oven
Sample Collector
Peristaltic Pump
Pump Tube
Waveguide Attenuator
Waveguide Attenuator
Slurry
Pump Head

Fig. 1. Block diagram of the prototype tube-based microwave digestion system.

A slightly-modified (Fig. 2), domestic-type, commercially available microwave oven (model EXR-1690C, Toshiba Corp., 1-1, Shibaura 1 - Chome, Minato-Ku, Tokyo 105) is utilized. The power is adjustable in 9 steps, from 1 ("Low" corresponding to a power of about 70 Watts) to 9 ("High" or "Full" which is equivalent to a power of approximately 700 Watts). The heating time is programmable via front panel push-buttons and can be set from 1 sec to 99 min and 99 sec.

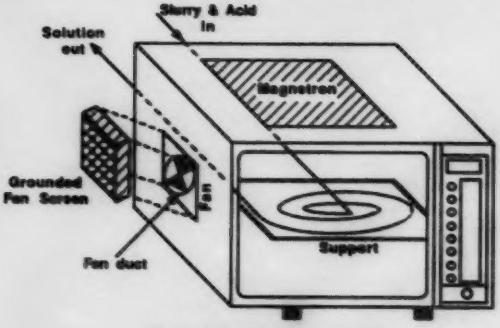

Fig. 2 Microwave oven set-up.

A Teflon PFA tube (perfluoroalkoxy, a chemically inert, nonporous tetrafluoroethylene with a fully fluorinated alkoxy side chain available from Cole-Palmer Instrument Co, Chicago, IL) with an ID of 1/4" and an OD of 5/32" serves as the digestion tube. According to manufacturer's specifications, it can withstand pressures of 421 psi and temperatures of 260° C. The tube, 13.8 ft (~420 cm) in length between the input- and output-valves, is coiled in 6 turns and is placed facing the magnetron, as shown in Fig. 2. This arrangement was chosen in order to take full advantage of the power delivered from the magnetron to the sample. A sample plug is pumped into the center of the coil. During digestion the sample slowly rotates inside the coiled tube due to pressure differences developed on either side of the sample plug. Fortuitously, this rotation serves as a stirring mechanism and also helps reduce the effects of non-uniform heating due to "hot spots".

After repeated use, for example, more than 100 times, the digestion tube showed visible signs of aging, such as yellowing, particularly at the T- and valve-joints and was replaced for safety reasons. In addition, a yellowish/brown coating and dark spots were visually observed inside the tube and in the interiors of the valves and the tube joints. These were attributed to undigested organic material. Some preliminary results indicate that the tube may have to be replaced more frequently due to accumulation of undigested material, which may give rise to memory effects, rather than due to aging or thermal/mechanical stress.

All measurements were performed using a Thermo Jarrel-Ash (Franklin, Massachusetts) model ICAP-61 inductively coupled argon plasma optical emission spectrometer. This computer controlled, 0.75-m, 34-channel polychromator system, is capable of determining 32 elements simultaneously.

C. Experimental

1. Reference Materials. The methodology was developed using "V85-1" and was tested using "Norway maple" and "White birch" botanical reference materials provided by the MOE (Rexdale facility). Although there are no certified values for these samples, the values reported here are the average quoted by the MOE. These were obtained using a 3 h long open-vessel digestion and analysis by ICP-AES [3]. Because the MOE and other environment monitoring laboratories are interested in trace elements that are environmentally available, their digestions are typically not brought to completion [4].

2. Procedure. Approximately 0.35 g of powdered sample is accurately weighed into a glass beaker and 20 mL of de-ionized water is added to it. The resultant slurry is continuously and rigorously stirred and then pumped, with both valves open (Fig. 1), into the digestion coil simultaneously with about 20 mL of acid or acid mixture. The valves are then closed and the sample is heated either at high power or using a power program (i.e., full power for 2 min followed by power level 5 for 3 min) for a pre-determined period of time. After digestion, the sample is allowed to air cool for several minutes. The exhaust valve is then opened to relieve pressure and the effluent is quantitatively transferred to the collection vessel.

Depending on power program and digestion time, the digests may contain unspecified amounts of undigested residue. Samples with residues are filtered, washed with distilled water, the filtrate is diluted to volume and analyzed by ICP-AES. All concentrations reported here are the average of five repeats and refer to dried samples. The moisture content was between 4% and 5%.

The digestion tube was thoroughly cleaned by a high speed flush with a water plug followed by a flush with an acid plug and a water plug. When changing sample types, the tube was cleaned by following the sample treatment procedure using only a water-acid mixture and by rinsing it with a water plug. The adequacy of this approach to eliminate memory effects is under investigation.

For the open-vessel work, approximately 0.35 g of sample were accurately weighed in an conical flask and mixed with 20 mL of distilled/de-ionized water and 20 mL of acid. The watch-glass covered flask was placed in a Pyrex vacuum desiccator (without the desiccant) which was subsequently placed in the microwave oven where it was heated for about 6 minutes. In order to vent acid fumes and to provide additional protection of the electronics and the magnetron, the vacuum port of the desiccator was connected to tygon tubing. The tube was routed, through one of the access ports cut on the back of the oven, to the fume hood. An open 100 mL beaker of water was placed in the oven in order to protect the magnetron from reflected power.

3. Safety. Safety was a key concern in operating this system. The following criteria were set: minimum radiation leakage (i.e., <5 mW/cm^2 measured at 5 cm from the oven or any tube or cable emerging from it), no acid fumes in the microwave cavity and maximum operating pressure and temperature of 125 psi and 230° C. Although the tube assembly was safely tested and briefly operated at pressures as high as 200 psi, the choice of a lower operating pressure for routine operation was dictated by the weakest links in the tube assembly, namely the tube-to-valve and the tube to T-joint connections. According to the manufacture's specifications this is only 125 psi.

Due to the modifications of the oven (i.e., access ports) radiation leakage was an important consideration and was extensively monitored using a sensitive microwave power meter. Typical values ranged below 0.2 mW/cm^2.

The final temperature of the sample in the digestion tube was measured in order to avoid placing excessive thermal stress on the tube. It was measured using a copper-constantan thermocouple encapsulated within a thin layer of glass and was held in place at about the middle of the digestion tube with a T-joint. The thermocouple leads were attached to a shielded and grounded cable. Regardless of power program and digestion time the temperature never exceeded the safety limit.

Due to the 125 psi pressure constraint, pressure was monitored in real-time. It was measured using a conventional pressure gauge and readings were manually taken at one minute intervals. The results for various acids, a 0.35 g of V85-1 botanical sample and high power are shown in Fig. 3. The steep slope observed when a mixture of HNO_3 and H_2O_2 are utilized indicates rapid formation of gaseous products and, although it may have to be correlated with temperature and H_2O_2 gaseous decomposition products, it also indicates a faster attack of botanical samples.

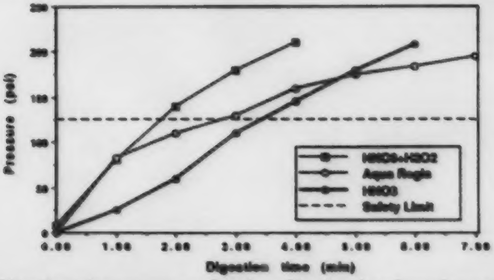

Fig. 3 Digestion tube pressure as a function of heating time for various acid mixtures.

From the results shown in Fig. 3 it can also be concluded that regardless of acid mixture, the 125 psi safety limit is reached in less than 3 min. And because aqua regia resulted in more complete digestions in the shortest time, it was the acid of choice and was used throughout.

However, when short digestion times are used (i.e., < 2 min) relatively large amounts of undigested material was visually observed to remain in the digestion tube and to settle in the collection vessel. Therefore, longer digestion times may have to be used in order to obtain a complete digestion (i.e., one that results in clear and colorless solutions with no visible signs of residue).

D. Results and Discussion

1. Power program and digestion time. A power program was utilized in order to increase the digestion time and to obtain a more complete digestion without exceeding the pressure limit. More specifically, V85-1 samples were digested by applying full power for 2 min followed by a lower power level for another 3 min. Pressure was monitored in real-time as before. The results are shown in Fig. 4. From these it can be concluded that there exists an almost linear relationship between applied power and pressure and that lower power levels result in longer digestion times, as expected. However, even when a power level 5 is used, resulting in an additional 3 min of digestion time, the amount of undigested organic material is still considerable.

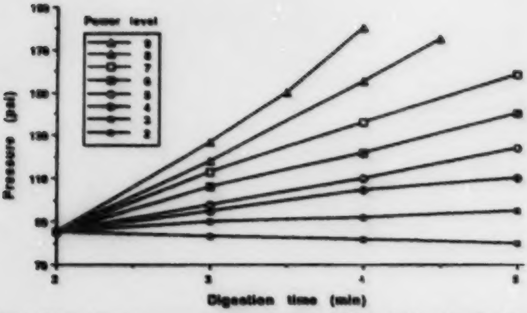

Fig. 4 Digestion tube pressure for various power levels (see text for discussion).

2. Power program and digestion time for complete digestion. The conditions for complete digestions were established by applying a series of power programs to V85-1 botanical slurries and aqua regia and by monitoring pressure in real-time. The experiment ended when all organic material was digested and a clear and almost colorless solution was obtained. The results are shown in Fig. 5. For power program 1 (Fig. 5, circles), high power is applied for 2 min, power is then turned off until pressure drops below 100 psi and high power is again applied until pressure exceeds 150 psi and so on until a complete digestion is obtained. For power program 2 (Fig. 5, squares), high power is applied for 2 min followed by the application of power level 4 for 7 min followed by power level 5 until the end of the digestion. Similarly, power program 3 (Fig. 5, triangles) is obtained by applying high power for 2 min followed by continuous application of power level 5 until the end of the digestion. From these results it can be concluded that program 3 results in a complete digestion in about half the time required by program 1, thus providing considerable time-savings. However, in terms of applied microwave energy, the power programs described above are essentially equivalent. This can be easily explained by considering programs 1 and 3. Excluding the initial 2 min period, full power is applied for a total of 10 min (program 1) whereas a power level 5 is applied for 20 min (program 3).

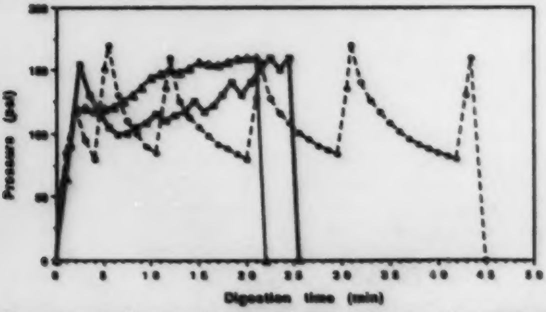

Fig. 5 Pressure versus digestion time for various power programs (see text for discussion).

However, a power level 5 is equivalent to a duty cycle of 50%, that is, full power applied half of the time. Thus, full power for 10 min is equivalent to power level 5 for 20 min. But, are complete digestions necessary in order to obtain 100% recovery of trace elements in botanical samples?

*3. **Elemental recoveries and digestion time.*** MOE V85-1 botanical samples were digested with aqua regia for 2-, 4-, 8-, 16- and 32-min. The digested samples were analyzed for Al, B, Ba, Cd, Cu, Fe, Mg, Mn and Zn. The results are summarized in Fig. 6. From these it can be concluded that trace metals are fully recovered in two minutes at full power when V85-1 samples are used. However, to further substantiate this conclusion, the question of individual elemental recoveries must be first addressed.

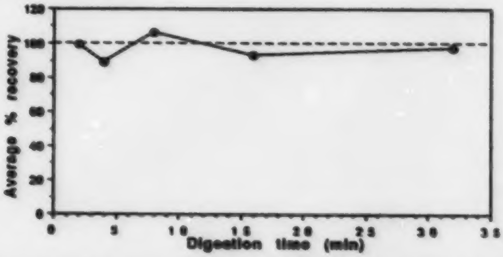

Fig. 6 Average recovery versus digestion time for V85-1 samples (see text.for discussion).

In order to test for the individual elemental recoveries, V85-1 samples were digested for 2 min at full power. The results are shown in Table 1. With the exception of Al which is under-recovered and of Ba which is over-recovered (both with respect to the MOE values), the average concentrations and the standard deviations are in agreement with the MOE values. No explanation can be offered at this point in time for the Al and Ba concentrations. In order to obtain "total" digestions and to establish a "reference" value, V85-1 samples are now being digested in the coiled tube for 32 min using a power program.

Table 1. Analysis of V85-1 reference botanicals.

Element	Coiled Tube (T) (μg/g)	Open (O) Vessel (μg/g)	MOE Value (μg/g)	% Recovery (T/O)	(O/MOE)	(T/MOE)
Al	54±5	56±3.9	100±11	96	56	54
Ba	13±0.4	14±0.3	10±0.7	93	140	130
Ca	12000±550	[illegible]00±470	12000±580	92	108	100
Cu	14±1	16±0.8	13±0.8	88	123	108
Fe	255±13	280±8.5	230±18	91	122	111
Mg	2300±88	2500±75	2100±130	92	119	110
Mn	67±2.5	68±2.0	60±4.6	99	113	117
Zn	140±6.4	160±0.4	140±11	88	114	100

In order to further substantiate the results obtained when short digestion times are used and to provide a basis for comparison [5], V85-1 samples were digested in the microwave oven using open-vessels (Table 1). From these results it can be concluded that the tube system recovers in 2 min about as much as open-vessels in 6 min, thus demonstrating the validity of our approach.

A comparison of short-time digestions with the MOE values reveals that, except for Al, the tube digestion system recovers in 2 min more than hot-plate digestions do in hours. From the low standard deviations reported in Table 1 it can be concluded that highly reproducible digestions are obtained with this system. Therefore, for a difficult-to-digest element, such as Al, a correction factor may be applied with a reasonable degree confidence. In summary, from the results presented thus far it can be concluded that for V85-1, a 2 min digestion provides elemental recoveries of about 100% for most elements.

4. Testing the methodology. The methodology developed thus far (i.e., aqua regia, 2 min digestion, full power) was tested using MOE Norway maple and White birch botanical reference materials. In order to verify the results obtained using the tube system and short digestion times, these samples were also digested in open-vessels. The results are shown in Table 2 for White birch and in Table 3 for Norway maple. In general, the results reported here are in good agreement with those reported by the MOE. In summary, and much like other microwave digestion systems [5, 6] elemental recoveries appear to be sample type dependent. However, more work remains to be done in order to further substantiate this conclusion .

Table 2. Analysis of Norway maple botanical samples.

Element	Coiled Tube (T) (µg/g)	Open (O) Vessel (µg/g)	MOE Value (µg/g)	% Recovery (T/O)	(O/MOE)	(T/MOE)
Al	130±19	100±5.8	180	130	56	72
Ba	18±0.76	18±0.59	14	100	129	129
Ca	28000±1700	28000±1100	28000	100	100	100
Cu	9.8±0.31	9.6±0.44	8	102	120	122
Fe	420±16	460±13	420	91	110	100
Mg	2500±140	2600±82	2200	96	118	114
Mn	56±0.1	53±18	47	106	113	119
Pb	120±4.1	130±3.4	95	92	137	126
Zn	42±1.9	44±1.6	40	95	110	105

Table 3. Analysis of White birch botanical samples.

Element	Coiled Tube (T) (µg/g)	Open (O) Vessel (µg/g)	MOE Value (µg/g)	% Recovery (T/O)	(O/MOE)	(T/MOE)
Al	24±2.6	24±2	42	100	57	57
Ba	84±0.95	100±3.4	86	84	116	98
Ca	14000±450	16000±370	14000	88	114	100
Cd	0.8±0.11	0.99±0.07	0.9	81	110	89
Cu	5.6±0.77	5.7±1.2	5	98	114	112
Fe	61±2.5	68±2.4	59	90	115	103
Mg	2100±75	2500±67	2100	84	119	84
Mn	611±16	704±19	600	87	117	87
Zn	180±8.5	220±7.3	200	82	110	90

E. Conclusions

In this preliminary study, a stopped-flow microwave digestion prototype system has been developed. Precise and quantitative digestions of trace elements in botanical samples are obtained in 2 min using straight forward methodology and inexpensive instrumentation. The methodology is being tested with NBS botanical and biological standard reference materials (SRMs). Initial results indicate that these SRMs can be easily digested in 2 min providing 100% recoveries for most elements. In order to test for a possible general applicability of stopped-flow digestions, this study is being further expanded to cover other sample types as well, for example, geological MOE and NBS SRMs. Some preliminary results show that even with short digestion times, the system can digest MOE soil samples and NBS coal fly ash. In this case, however, the acid mixture must also contain 1 to 2 mL of HF.

The current shortcomings of the system stem from the use of relatively large volumes of acids, from tube contamination with consequent memory effects and from delays arising during cooling the digests. These are under study and appear to be easy to solve. The additional safety precautions required for routine operation, for example, installation of waveguide attenuators in all access ports and a pressure release valve (Fig. 1) are also being addressed.

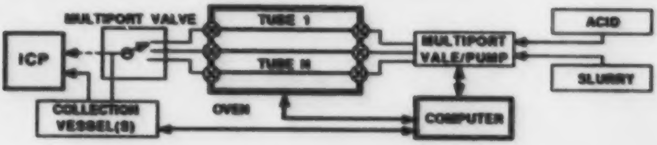

Fig. 7 Diagram of the proposed 'next generation' stopped-flow digestion system.

The findings reported here and the experience gained in operating this system will be used as the basis for the development of a computer controlled system operating asynchronously on multiple tubes/samples (Fig. 7). This system will be subsequently tested with some difficult-to-digest samples, such as soils and geologicals. Further into the future, automation of sample handling, preparation of slurries and even a direct interface to the ICP are envisaged (Fig. 7). Development of such a system is anticipated to give rise to an intelligent sample processor for the ICP [7].

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D14

AN ELECTROTHERMAL VAPORIZATION SYSTEM FOR THE DIRECT ANALYSIS OF SOLIDS BY ICP-AES

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BACKGROUND

In our laboratory we have studied sample introduction systems for atomic spectrometry for over a decade. The original work centered on the use of DSI (Direct Sample Insertion) techniques. These techniques involve inserting a sample carrying probe into the plasma along the axial channel. Our original work was with liquid samples using wire loops [1] and electrochemical preconcentration techniques [2]. This work provided the background for a move into direct solid sample analysis by DSI for both atomic emission [3] and mass spectrometry [4].

Considerable solids oriented work on the DSI using both cups and wire restrained pellets has demonstrated that the technique has very low detection limits, yet requires the use of standard additions in cases where the matrix is complex [5-7]. At the onset of the project, we targeted geological materials. These often have a silicon matrix and so require considerable sample preparation, often with HF, and consequently were considered appropriate candidates. If the material is inserted into the plasma in a graphite/sample pellet with a high proportion of the analyte, a Si cloud will carry a great deal of the analyte through the plasma without excitation. The large Si vapor cloud appears to alter normal flow patterns in the plasma and changes the excitation conditions. However, volatile toxic elements (i.e., Cd, Hg and Pb) emerge before the Si cloud and are measurable. Dilution of the sample in more graphite results in much better accuracy but drastically reduces detection limits since less sample is introduced into the plasma.

In an attempt to modify the chemistry of the system, we have used various additives including AgCl, NaF and CuCl to produce volatile halides. The NaF causes a rather spectacular breakdown of the Si in a short time but again causes significant disruption of the plasma while carrying a great deal of the analyte with it.

To summarize, we felt that a number of general lessons were learned that could be applied in the development of a new type of solid sample introduction system.

1. Large amounts of analyte should be vaporized. This improves detection limits in proportion to the mass of the analyte (disregarding the interference effects mentioned above).
2. The vapor must be forced through the center of the plasma.
3. The vapor should be generated in such a way that it causes a minimal disruption of the plasma.
4. Chemistry can be used to modify the sample breakdown processes, but must not be allowed to distress the plasma.

In the following section we will discuss the results obtained with a system designed with the above lessons in mind.

RATIONALE

Given the requirements for large mass and minimal disruption of the plasma, we developed a system which uses the "Separate Sampling and Excitation" principle implemented so well in the Thermo Jarrell Ash® Spark (sampling)/ICP (excitation) system. Unfortunately, the spark in these systems only vaporizes a relatively small portion of the sample, resulting in relatively high (poor) detection limits. Our approach involves electrothermal heating of a graphite/sample pellet. The ETV (electrothermal vaporization) configuration, Figure 1, allows the sample to be "processed" remotely from the plasma. Analyte vapor is then transported to the plasma where the use of a traditional torch/injector configuration forces the vapor cloud through the center of the plasma. The use of a pellet, rather than the conventional sample cup or tube, allows large amounts of sample to be heated very rapidly due to the intimate contact between the resistively heated graphite and the sample.

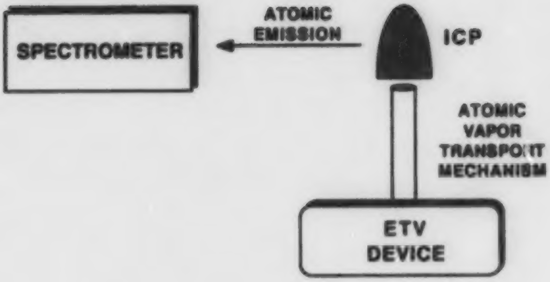

Fig. 1 Illustration of "Separate Sampling and Excitation".

EXPERIMENTAL

The ETV apparatus is illustrated schematically in Figure 2. The present configuration is a first prototype and was developed with the primary goal of expediency. A conventional Perkin Elmer HGA 2200 furnace assembly was used nondestructively by adding the components illustrated in Figure 2. Our goal was simply to test the principle, and no particular attention was paid to the gas flow patterns. We did place the pellet in between the entrance and exit gas ports, however, we expected that there would be considerable "dead volume" in an unswept design such as this.

Pellets were hand pressed into a 4 mm diameter cylinder 9 mm long using a Parr press and Spex spectroscopic grade dc arc graphite in a ratio of 9 graphite to 1 sample. The pellets are ramped through a short drying cycle to remove moisture and then raised rapidly to 1250°C to produce a short duration analyte pulse in the plasma. A temperature of 100°C was used for standards (oxides) while 300°C was used to ash botanical samples. MOE V85-1, Norway Maple and White Birch samples were used to evaluate the samples with real samples.

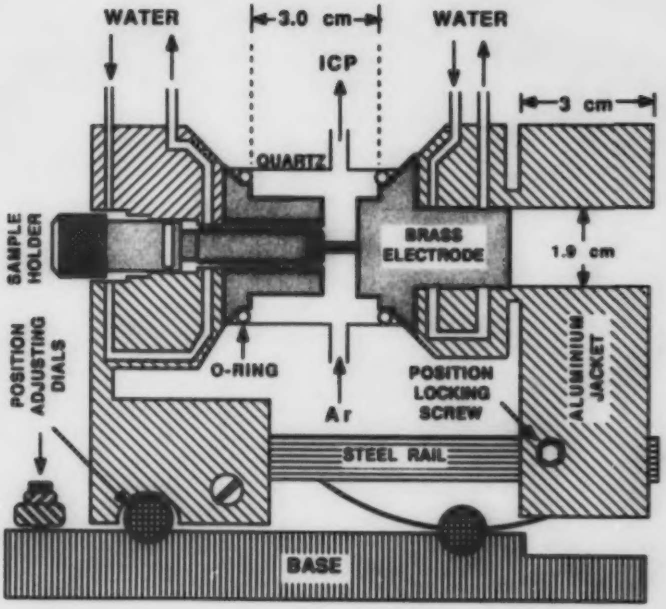
WATER
3.0 cm
ICP
WATER
3 cm
QUARTZ
SAMPLE HOLDER
BRASS ELECTRODE
1.0 cm
POSITION ADJUSTING DIALS
O-RING
Ar
POSITION LOCKING SCREW
ALUMINIUM JACKET
STEEL RAIL
BASE

Fig. 2 Illustration of ETV device.

Measurements were made on an older Jarrell Ash simultaneous multichannel spectrometer modified by Technical Services Laboratory of Toronto. The modifications included the addition of a galvanically driven refractor plate with direct computer control over the drive and data acquisition. Both the DSI and ETV experiments produce analyte clouds in a very narrow time window. The modified spectrometer system allows very rapid on and off line measurements which are often essential to this type of work. The software/hardware in this configuration provides a degree of flexibility which is not possible in commercial systems with which we are familiar.

PERFORMANCE

Exemplary detection limit data for several elements in single element mixtures are presented in Table I. Precision data is presented in Table II for standards. Both are obviously very encouraging. We find it very gratifying to have solid detection limits which are comparable to those obtainable with liquid techniques. Note that the Jarrell Ash plasma detection limits are for liquid samples. To digest a sample, a factor of roughly 10 in dilution would be expected subsequently raising the detection limit in the solid by a factor of 10.

Table I. Detection limits.

	Pellet-ETV system		Jarrell Ash ICAP 61	
Element	Line (nm)	DL (ppb)	Line (nm)	DL (ppb)
Pb	220.3	4.4	220.3	26.5
Zn	425.4	17.0	213.8	0.4
Cd	228.8	5.0	228.8	0.7

Table II. Reproducibility.

Element	Peak Height (%RSD)	Peak Area (%RSD)
Pb	4.0	4.9
Zn	3.0	*
Mn	9.5	13.7
Cd	5.5	8.2

* No data available due to multiple peaks

Typical time profiles are presented in Figure 3. It is interesting to note that many of the elements evolve at quite different times. This is similar to what we have observed with our DSI system. We generally consider this beneficial, since it allows the spectral interference from one element to pass through a different time window. It is important to note, however, that real sample matrices may drastically alter the time performance and nullify this apparent advantage. These experiments were run with a final temperature of 1250°C, higher temperatures may force the analytes out more quickly. This could be advantageous in overcoming matrix effects, but may also result in an unwanted pressure pulse. The system may also allow us to use matrix modifiers such as NaF without the disruption to the plasma which we experienced when using DSI probes in the plasma.

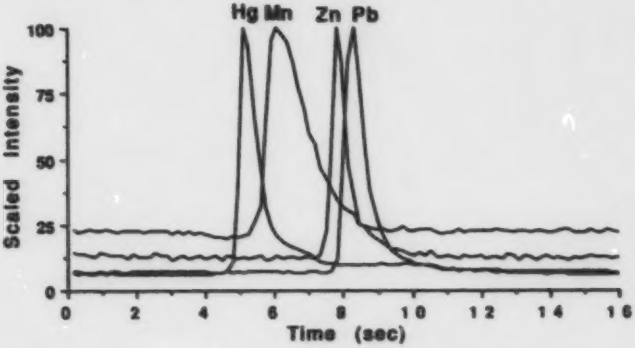

Fig. 3 Typical analyte emission temporal behavior and "volatility" sequence.

Table III. Analysis of MOE botanical reference materials for Pb and Zn.

	Element: Pb		Element: Zn	
Sample Type	Found Conc.	MOE Value	Found Conc.	MOE Value
V85-1	17 ppm	19 ppm	46 ppm	14 ppm
White birch	350 ppb	400 ppb	58 ppm	20 ppm
Norway maple	42 ppm	40 ppm	48 ppm	40 ppm

We tested the system on several MOE sample types for two elements, Zn and Pb (Table III). These first results are quite encouraging, although our experience [5, 6] would lead us to expect that botanical samples should be relatively easy sample types. Our next step will be to explore more difficult sample types such as the geological MESS and BCS or NBS Coal Fly Ash. These will provide an interesting test of the Separate Sampling and Excitation principle as applied to ETV vaporization.

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FLOW INJECTION PRECONCENTRATION/DIRECT SAMPLE INSERTION FOR TRACE ANALYSES BY ICP-AES AND ICP-MS

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INTRODUCTION

As our knowledge of the environment increases, our need for better analyses grows. The inductively coupled plasma using either optical or mass detection, would appear to an option worth exploring. However, to be of maximum value, the detection limits of the ICP-AES need to be improved and the ICP-MS suffers from serious matrix effects. We have undertaken the development of a system which combines two technologies, flow injection analysis (FIA) and direct sample insertion (DSI) to obtain sample clean up and detection limit improvements. If successful, this system will extend working ranges and minimize matrix effects for both types of instrumentation.

The union of flow injection analysis (FIA) with inductively coupled plasma atomic emission spectrometry (ICP-AES) has been reported in the literature [1-6]. Standard pneumatic nebulization using cross-flow or concentric nebulizers are usually directly coupled to the output of the FIA system. This has given good results but the small discrete plug from the FIA is diluted in the spray chamber. It is the low transport efficiency (reported to be between 1-5%[2]) of these nebulizers that has lead Gustavsson to remark; "Consequently an interface between an FIA device and the ICP, capable of utilizing the full potential of the combination, has yet to be developed."[3]

LaFreniere and co-workers have developed a direct injection nebulizer (DIN) that achieves 100% sample introduction efficiency and is compatible with typical FIA flow rates. They report some detection limit improvements but it seems to suffer from solvent loading problems.[4,5]

Thermospray interfacing, which has been used to combine liquid chromatography with mass spectrometry, has also been applied to FIA/ICP-AES. With thermospray the liquid effluent is forced through an electrically heated stainless steel capillary producing a super heated aerosol carried in a jet of vapour. Some detection limit improvements were reported but the system is still undergoing design changes.[6]

Electrothermal vaporization (ETV) has not yet been reported in combination with FIA. It has however been well established as a sample introduction method for small volume liquid samples to ICP-AES using both graphite tubes,[7] wire loop atomizers[8] and metal filaments[9]. In ETV, control of the drying step is possible.

In our original proposal we presented direct sample insertion as a viable way to introduce pre-concentrated samples from our FIA system to the plasma. Newly designed graphite cups of overall reduced mass have been described as being able to achieve an order of magnitude improvement in detection limits.[10] As reported by Sing and Salin, wire loops give detection limit improvements of 1-2 orders of magnitude based on one drop.[11] Since we hope to be able to collect the total volume (approx. 100 -250 uL.) from the FIA and dry it onto the loop (or into the cup), essentially another pre-concentration, our detection limits compared to nebulization of this small volume should be improved to an even greater extent.

Table 1 compares the three ways of introducing liquid samples to the ICP.

Table 1 Discrete Liquid Sample Introduction Techniques for ICP-AES

Method	Advantages	Disadvantages
Wire loops	Superior detection limits	Spectral interferences (W loop)
	Already interfaced with the ICP-MS at the MOE	Difficult interface -possible loss of sample -long drying times
	No carbide formation Time resolution of elements	
Graphite cups	Easy interface	Carbide formation with refractory elements
	- batch mode drying	
	Specially machined cups x 10 better detection limits	Overall detection limits higher than wire loops
ETV	Maximal control of drying conditions	Carbide formation
	Easy interface Good detection limits	Some memory effects observed

EXPERIMENTAL

Flow Injection Analysis System Developed

The FIA system shown in Figure 1 is based on the chemistry of preconcentration of Chelex-100 ion exchange resin with a strong acid as the eluent. A recent critical examination of Chelex-100 for the enrichment of sea water found it to be a good choice if enough attention is given to several critical parameters.[12] This has also been our experience and the applicability of Chelex-100 to a wide range of target metals, as well as its ability to reduce matrix effects by selectively rejecting cations such as Na, Ca and Mg, make it a good candidate for several sample types.

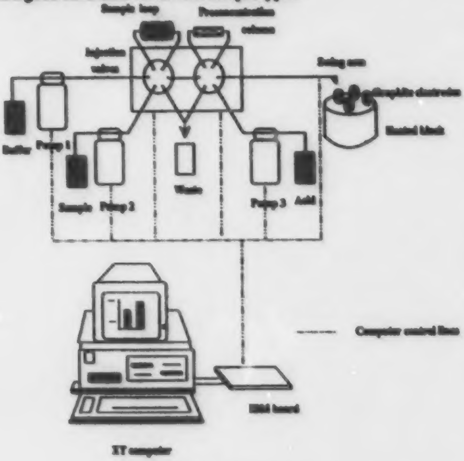
Sample loop
Preconcentration column
Injection valves
Swing arm
graphite electrodes
Heated block
Buffer
Pump 1
Sample
Pump 2
Waste
Pump 3
Acid
Computer control lines
XT computer

Figure 1. Flow Injection System Developed

There has recently appeared on the market a preconcentration unit, to be used as a front end to an ICP-AES spectrometer, marketed by Dionex Corporation. The column used in this system contains a resin with the same macroporous polystyrene-divinylbenzene iminodiacetate backbone as Chelex-100 but with a higher degree of crosslinking. It is this higher degree of crosslinking that solves some of the difficulties such as the 100% swelling that Chelex-100 undergoes with a change in pH.[13] For this reason columns based on this resin will also be evaluated. The similarity between the resins means that the optimal experimental parameters are comparable.

DSID Sample introduction

Graphite cups

Standard graphite cups such as those used by Shao and Horlick[14] were first tried with the stepper motor direct sample insertion device as described by Sing and Salin[11]. The spectrometer used was a Thermo Jarrell Ash multi channel with software and hardware modifications made by Technical Services Laboratory[15]. The operating conditions are listed in Table 2. The detection limits, as discussed in former reports, obtained without optimization were comparable or an order of magnitude worse than those obtained by nebulization with the same system.

Umemoto and Kubota recently reported on the results of using specially machined graphite cups with relatively thin walls (0.5 mm) and approximately 1 mm diameter supporting rods. They found an order of magnitude increase in detection limits over pneumatic nebulization.[10]

The dimensions of the thin walled graphite cup as compared to that used previously are given in Table 2. Preliminary experiments with graphite cups that had only a 1 mm stem thickness indicated that they would be too fragile for routine work. The graphite rod thickness used was 2 mm which gave slightly lower signal levels, on the order of 5%, and were considerably more robust.

Table 2 ICP Operating conditions (Graphite cup)

Spectrometer	Thermo Jarrell Ash (modified by TSL laboratories)		
ICP parameters		**DSI parameters**	
Forward power	1.25 kW	Drying height	25 mm below TOLC
Reflected power	< 50 W	Drying time	30 sec
Plasma gas flow rate	14 L min^{-1}	Insertion depth	2 mm above TOLC
Aux. gas flow rate	0.8 L min^{-1}	Insertion time	45 sec
		Observation hgt	15 mm above TOLC

Cup Dimensions:

	Conventional	Thin walled
Cup depth(mm)	4.8	6.0
Rod thickness(mm)	3.2	2.0
Wall thickness(mm)	0.8	0.5
Cup diameter (mm)		
i.d.	4.57	5.18
o.d.	6.0	6.0

* TOLC = top of the load coil

Wire Loops

The wire loops used were formed from rhenium wire, instead of the tungsten used by Sing and Salin in previous work[11], as a means to reduce potential spectral interferences.

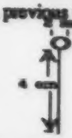

Figure 2 Re wire loop

The wire was 0.5 mm in diameter and was formed into two side-by-side 2 mm diameter loops on the end of a 4-cm stem, this is similar in dimensions to the traditional W loop (see Figure 2). Ten uL samples were applied with a Eppendorf pipet. The rest of the operating conditions are listed in Table 3.

Table 3 ICP Operating Conditions (Wire loop support)

Spectrometer	Thermo Jarrell Ash (modified by TSL laboratories)		
ICP parameters		DSI parameters	
Forward power	1.5 kW	Drying height	22 mm above TOLC
Reflected power	< 50 W	Drying time	20 sec
Plasma gas flow rate	14 L min^{-1}	Insertion depth	2 mm above TOLC
Aux. gas flow rate	0.8 L min^{-1}	Insertion time	5 sec
		Observation hgt	15 mm above TOLC

RESULTS AND DISCUSSION

Flow Injection System

The full details of the preconcentration chemistries attempted have been previously reported[16]. To recap; the ion exchange resin, Chelex-100 was evaluated with both acid elution and the use of other complexing agents as eluting agents. Nitric acid elution gave pre-concentration factors of 33 for Cu, 22 for Cd and 24 for Zn. When EDTA was used as the eluent, respective enrichment factors of 24 and 22 were obtained for Cd and Pb. The best pre-concentration factor, a value of 50, was obtained when L-cysteine was used to elute Cu from the column. The only caveat in this case is that a reduction step makes this application element specific.

Direct Sample Insertion

Thin-walled Graphite Cup

The results obtained with the thin-walled graphite cup indicate that there are detection limit improvements both over regular nebulization and standard graphite cups. The detection limits are reported in Table 4.

Table 4 Detection limits with Thin-walled Graphite Cup (ppb)

Element/	Line (nm)	Pneumatic Nebulization	Graphite Cup (thin walled)
Cu	324.7	8.4	0.86
Cd	228.8	9.3	2.1
Pb	220.3	28	0.85
Zn	425.4	82	0.62

* peak area, 50 uL samples
3 sigma detection limits

Wire loop

The first results obtained with the rhenium wire loop indicate that it is a good alternative to tungsten. There was no interference observed for a blank of distilled deionized water at the wavelengths of any of the elements analyzed (Cd, Cr, Cu, Mn, Pb, V, Zn).

The preliminary detection limits are shown in Table 5. It should be noted that the results on the rhenium loop were not obtained under optimized conditions. A factor of improvement between 3 and 4 was obtained for most elements. There is every reason to expect that, with optimization, a factor of 10 (ie. that found by Sing and Salin) improvement in detection limits will be realized.

The rhenium loop was inserted into the plasma more than 60 times over the time period of these initial experiments with apparently no deterioration of the loop. In this way, it proves to be a better material than tantalum.

Table 5 Detection limits with Wire Loop (ppb) * peak area, 10 uL samples

Element/	Line (nm)	Pneumatic Nebulization	Wire loop (rhenium)
Cr	267.7	28	9.2
Mn	293.9	7	2.2
Pb	220.3	28	7.3

FIA Combined with DSI

The flow injection system, as shown in Figure 1, was used to preconcentrate 5.0 mL of standard aqueous solutions into an acid matrix which was collected and then dried into a thin-walled graphite cup using an infrared lamp. The preconcentration column used contained either Chelex-100 (100 -200 mesh) or the MetPac CC-1 resin (50-100 um) as developed by Dionex. The length of the column was 2.0 cm with a 2.30 mm inner diameter constructed from Tygon tubing. The buffer used was 0.5 M ammonium acetate (pH = 5.5) at a flow rate of 2.0 mL; the acid is nitric (2.0 M) at a flow rate of 1.2 mL min^{-1}

The control program was written in Turbo Pascal 5.0 and allows for a flexible interface that uses an IBM 16 port I/O board to control up to 16 pumps or valves. Each step in the preconcentration process involves having the valves in a certain position and the pumps operating or not. Our input data files specify both the status of the pumps and valves and the length of time for the system to remain at that status. After the time has passed, as determined by external computer timing, the status of the pumps and valves is altered. The program used to preconcentrate the 5.0 mL sample volume is laid out in Table 6.

Table 6 Preconcentration program

time (sec)	V1	V2	P1	P2	P3	Action
150	1	0	0	1	1	1. Loading the sample loop and rinsing the column with acid
120	1	1	1	0	0	2. Conditioning the column with buffer
150	0	1	1	0	0	3. Loading the sample onto the column.
110	1	0	0	0	1	4. Eluting the column with acid and collecting the preconcentrated sample.

1 = ON / LOAD
0 = OFF / INJECT

Initial results with the combined system are positive. However, there seems to be considerable tailing of the elution peak which results in the analyte being over a greater volume. Future efforts will be concentrated on reducing the acid eluent volume by altering the column dimensions, shortening the connecting tubing and increasing the acid strength and/or flow rate.

CONCLUSIONS

The chemistry of preconcentration by flow injection analysis has been aptly demonstrated to work. The preconcentration factors vary with the amount of sample and time available and, of course, the experimental parameters.

Future work will concentrate on gathering the detection limit improvement data using standard samples. The FIA-DSI approach will also be applied to several real sample matrices to demonstrate some of its potential applications.

Direct sample insertion is a viable means of ensuring that one hundred percent of the mass of the desirable elements in the target sample are delivered to the plasma; freed by FIA from the interferents that may have originally been present.

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Prereduction of Arsenic(V) to Arsenic(III), Enhancement of the Signal, and Reduction of Interferences by L-Cysteine in the Determination of Arsenic by Hydride Generation

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Since Holak [1] published his paper on the determination of arsenic by hydride generation-atomic absorption spectrometry, many papers have been published which deal with arsenic determination by arsine generation combined with AAS [2-6], ICP-AES, [3,4,7] and DCP-AES [8-10]. Since trivalent and pentavalent arsenic show different behaviour in the arsine generation process, several workers [11-14] have developed methods for selective determination of As(III) in the presence of As(V). On the other hand, because of the difference in sensitivity between the As(III) and As(V) in the hydride generation process,[15,16] many workers have preferred to reduce As(V) to As(III) with various prereducting agents before arsine generation. The most popular prereductant is potassium iodide. It has been used in combination with ascorbic acid, which can prevent the oxidation of I^- to I_3^- by air or some other oxidant such as Fe(III)[17]. However, KI can only be used in strong acid media. The acid concentration is critical, for example, at concentrations of less than 0.3M, it failed to reduce As(V) to As(III) completely.[13,17] Furthermore, some workers reported that, when using KI as prereductant, it took as long as 4-5 hours to reduce As(V) to As(III) completely at room temperature.[17,18] Potassium iodide has also been used in combination with sodium sulphite,[19] and with thiourea.[20] Thiourea alone has been used in dilute acid[13] but caused competing reactions in the later hydride generation step. Takahashi *et al.* [22] reported that , when mercaptoacetic acid was used as a prereducing agent, the sensitivity in the determination of inorganic arsenic by atomic absorption spectrometry was lower than when potassium iodide was used.

For applications other than hydride generation, other prereducing agents have been used. Sodium thiosulphate alone [23] and in combination with sodium hydrogen sulphite,[24] and titanium(III) chloride[25] have been used to reduce arsenic(V) to arsenic(III) in solvent extraction methods that have been used in speciation studies. Sodium sulphite has been used in stripping voltammetry.[26]

In our previous work, [10, 27] we found that, when hydride generation was allowed to proceed for 20-30 seconds in 5 M HCl before arsine was stripped, peak heights may be used to determine the total (As(III) and As(V)) arsenic concentration. A delay column was necessary, for determination by DCP, to control the surge of hydrogen which would otherwise destabilize the plasma.

Although the hydride generation technique is relatively simple and has high sensitivity, it suffers from interferences that arise from certain metal ions in the sample solution.[15, 28-32] We have found that L-cystine and L-cysteine are excellent reagents to reduce interferences in the hydride generation process for the determination of arsenic,[27] tin,[33] and germanium.[34, 35] In addition, we have shown that L-cysteine can speed up the rate of reduction by sodium tetrahydroborate (III), thereby increasing the sensitivity in the determination of Ge.[34]

In this paper, we report our investigation of the characteristics of L-cysteine as a prereducting reagent for As(V). We also report a method to determine total inorganic arsenic at low acid concentration with a flow-through batch hydride generator in which L-cysteine acts, not only as a prereducing agent, but also also as a reagent which reduces interferences and also increases sensitivity.

Results and Discussion

L-Cysteine Enhances Signals

We have shown that acid concentration is critical in the determination of other elements by hydride generation [33, 34]. Thus we have investigated the effect of acid concentrations on the generation of arsine in the presence and absence of L-cysteine. In the absence of L-cysteine, the production of arsine, measured as peak height, increases steadily as the acid concentration increases, and reaches a plateau when the acid concentration reaches 0.08 - 0.10 M. In the presence of L-cysteine, on the other hand, arsine production reaches a maximum over a range of acid concentrations from 0.01 to 0.03 M. Over the best range of acid concentrations, the peak heights, where L-cysteine were used, are some 75% greater than peak heights obtained in 0.1 M acid in the absence of L-cysteine. No significant difference in behaviour was observed when nitric acid or hydrochloric acid was used as the acid medium.

Prereduction of As(V) by L-Cysteine

When studying the effect of L-cysteine on arsine generation from As(V), it was found that, over the range of acid concentrations from 0.01 - 0.02 M, no arsine was detected in the absence of L-cysteine. Measurement of the pH showed that, after 5 ml of the test solution reacted with 1 ml 2% m/V $NaBH_4$ solution (stabilized with 0.8% m/V NaOH), the final pH value was greater than 8. It was not surprising, therefore, that no arsine was released from the As(V) solution since As(V) has been reported to be reduced to arsine only in a strong acid medium.[11-12] When L-cysteine solution was added to the arsenic(V) solution just before the $NaBH_4$ solution was added, almost no arsine was measured. If the solution was allowed to stand, the signal gradually increased with time. This phenomenon suggested that L-cysteine probably plays a role as a prereducting agent which reduces As(V) to As(III) and is itself oxidised to L-cystine. At room temperature and in 0.02M acid medium, the reduction of As(V) to As(III) was complete within 35, 60 and 135 min. when L-cysteine (1 g, 0.5 g and 0.25 g respectively) was added to 100 ml of 50 ng ml^{-1} As(V) solution. When the solution in the 0.02M acid medium was heated in boiling water for only 5 minutes, As(V) was completely reduced to As(III). Heating for as long as 45 mins resulted in no arsenic loss. In addition, when prereduction was carried out in 1M acid with 0.5 g L-cysteine at room temperasture, As(V) was completely reduced to As(III) within 5 min. Compared with the other systems tested, L-cysteine seems to be an excellent reagent for the prereduction of As(V).

Speciation

Since L-cysteine reduces As(V) to As(III) slowly at room temperature and at low acid concentration, it was felt that it might be possible to determine As(III) in the presence of As(V).

Thus, a solution containing As(III) and As(V) was injected into the generator; L-cysteine solution was then added, followed immediately by the $NaBH_4$ solution. In this way, only As(III) reacts to form arsine. A separate sample can be reduced with L-cysteine prior to the hydride generation step to give the total As(III) and As(V) concentration. Acid and $NaBH_4$ concentrations are critical factors for reducing As(V) interference in the determination of As(III). The best conditions for the determination of As(III) in the presence of As(V) are as follows: 1 ml of 2% m/V of L-cysteine is added to 5 ml of the solution of As(III) and As(V) in 0.01M HCl, immediately followed by addition of 1 ml of 0.5% m/V $NaBH_4$. Under these conditions, 2.5 µg As(V) did not interfere in the generation of arsine from 250 ng As(III).

Interference Studies

When studying interference, 1 ml of the interfering ion, at different concentrations, was directly added to the generator containing 5 ml of arsenic(III). The signals obtained in this way were compared with those where no interfering ion been added. Table 1 shows the interference of some transition elements and the interference-reducing effect of L-cysteine.

Table 1. Interference from Transition Elements and the Effect of L-Cysteine

Metal Ions	Concentration (µg ml^{-1})	Recovery (%)	
		No L-Cysteine[a]	With 0.5% m/V L-Cysteine[b]
Au(III)	0.2	95	102
	2	78	91
	20	8.0	77
Pt(IV)	0.2	100	100
	2	55	96
	20	2.0	92
Pd(II)	0.2	76.	92
	2	n.d.[c]	94
	20	-	85
	200	-	54.
Ag(I)	0.2	-	105
	2	87.	101
	20	42	95

	200	-	87
Ni(II)	0.2	76	-
	2	11.5	98
	20	-	66
Co(II)	0.2	82	-
	2	25.8	-
	20	-	98
	200	-	64
Cu(II)	0.2	82	-
	2	67	-
	20	12.4	101
	200	-	96
Fe(III)	20	93	104
	200	-	99
Fe(II)	20	36	99
	200	-	99
	2000	-	91
Hg(II)	2	-	99
	20	95	103
	200	-	105
Mn(II)	20	91	99
	200	-	100
Zn(II)	20	65	99
	200	-	96
Cr(IV)	2	-	99
	20	101	102
	200	87	94
Cd(II)	20	96	102
	200	-	96
Mo(VI)	2	102	105
	20	189	98
	200	-	96

[a] The concentration of As(III) was 50 ng ml^{-1}.

[b] The concentration of As(III) was 125 ng ml^{-1}

[c] n.d. - not detected

Without L-cysteine, Pd, Pt, Au, Ag, Ni, Co, Cu, and Fe interfere with the hydride generation process and the interferences were more severe than in 5 M HCl medium,[27] which agrees with the findings of Welz and Melcher.[30] Moreover, the interference resulted in a memory effect. Interfering ions, introduced to the generator in a determination, would depress the arsenic signal of the next determination even in the absence of interfering ions. This could be due to a residue of finely divided metal particles, precipitated on the generator, which was not completely removed during the cleaning. Interference in the generation of the hydride by finely divided metal has previously been reported by Welz and Melcher.[32] Molybdenum was exceptional in that, in the absence of L-cysteine, enhanced recovery of arsenic was observed. The interference-free level of the above elements that could be tolerated was increased by one, two, and even three orders of magnitude, due to the presence of L-cysteine, and there was no observable memory effect. Compared to L-cystine in 5 M HCl,[27] L-cysteine, even in 0.02 M HCl, reduced interferences more effectively from gold and paladium, though it was less effective in reducing interferences from cobalt and nickel. In addition, at the low acid concentrations used, L-cysteine, readily dissolves in solution and thus simplifies the method.

Table 2 shows that, except for tellurium and selenium, other hydride forming elements, at concentrations up to 20 μg ml^{-1}, have no influence on arsine generation in the system. It is also interesting to note that tellurium and selenium interfere more severely when L-cysteine is present than when it is absent.

Table 2. Interference of Hydride Forming Elements and the Effect of L-Cysteine

Ions	Concentration (μg ml^{-1})	Recovery (%)	
		No L-Cysteine[a]	With 0.5% m/V L-Cysteine[b]
Bi(III)	2	96	102
	20	75	101
Ge(IV)	2	94	101
	20	95	102
Sb(III)	2	-	101
	20	100	101
Sn(II)	2	-	98
	20	101	99

	200	-	100
Pb(II)	2	76	97
	20	56	100
Se(IV)	0.2	-	97
	2	106	94
	20	100	78
	200	63	7.7
Te(IV)	0.2	96	100
	2	100	53
	200	67	10.4

a. The concentration of As(III) was 50 ppb.
b. The concentration of As(III) was 125 ppb.

Detection Limit and Precision

The limit of the detection for As(III) (three times the standard deviation of the blank) was 0.62 ng ml^{-1} for a 5 ml sample. The relative standard deviation of ten determinations of 50 ng ml^{-1} As(III) was 1.1%.

Conclusion

The present study has shown that L-cysteine plays a three-fold role in the determination of total inorganic arsenic by means of hydride generation. First, it is an efficient prereducing agent compared with other prereductants. It can prereduce As(V) to As(III) completely in the low acid concentration required by the arsine generation reaction. Secondly, the arsine signal is increased by 75% in the presence of L-cysteine. Thirdly, interferences from foreign ions are significantly reduced due to the presence of L-cysteine. In addition, L-cysteine shifts the optimum acid concentration for arsine generation to 0.01 - 0.03 M, thus reducing the amount of hydrogen produced, which is beneficial in DCP-AES determination. The method can be used to determine trace concentrations of arsenic in difficult sample matrices.

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VOLUME II

SESSION D

ANALYTICAL METHODS RESEARCH

POSTER PRESENTATIONS

EXPERT SYSTEMS IN ANALYTICAL CHEMISTRY. DESIGN OF A USER INTERFACE AND IMPLEMENTATION OF RULES FOR ACdiagnosis WITHIN ACexpert.

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Abstract This paper describes the application of expert system technology to analytical chemistry as part of the development of the ACexpert system. An expert system can be defined as a computer program that achieves a high level of performance in areas that otherwise require years of special education and training. In a rule based expert system knowledge is expressed in the form of conditional if-then rules. Here the main emphasis is on the power of reasoning, that is, the relations between facts rather than the facts themselves. The most widespread control applications of expert systems have been in diagnostics, in support of operators during disturbances (1,2).

DESIGN OF A USER INTERFACE FOR ACexpert

ACexpert is an expert system that deals with automated trace metal analysis by atomic absorption spectrometry (AAS). ACexpert is subdivided into individual expert system modules designed to perform specific tasks (3). The complexity and breadth of analytical chemistry means that ACexpert must be capable of interacting with several different modules, some rule based, some procedurally based, and some graphically based. To achieve this degree of flexibility, we have designed a general purpose user interface which can handle real-time problems , and at the same time will be able to provide access to any type of module.

Expert systems rely on data, these data will often be held in remote databases. As a result of regulations, large amounts of environmentally important analytical data are stored in databases. Over a number of years, these databases become so big that it is not possible to read these data without proper computer-aided "browsers". Because these database systems can be very large, decisions on the proper way to access the data are critical in the design of the ACexpert system. So, it is very important to add mathematical functions into the system which can convert the data into graphical representations. Based on all these requirements, the prototype of the ACexpert interface becomes very complex. After various tests, we decided to use Microsoft Windows 3.0 using ACTOR, an object oriented program, to help with the code writing. With these tools in hand, it is much simpler to design the interface. By adding different menus into different levels of windows, and by using the MOUSE, it becomes less difficult for the user to interact with the system and to handle real time problems. In our system, it is possible for the user to leave one window open, which could be showing a graphical display, and then open a second window to carry out calculations, the user can open third level windows to carry out rule based inferences. Also, it is possible to pass the results which are obtained from the calculation window to another window, and then to represent the data in the graphics window.

It is also very important to find a way to access a particular data file inside the database system. In order to solve this problem, a proper set of chemical knowledge is added to the system, so that the user can specify the type of data to be accessed within the database system. For example, if the user wants to open a data file, the system will first display a dialogue box which asks the user to fill in the necessary information, the system can then decide by itself which file the user is interested in and can display this data file in a display window. If the user does not know all the necessary information which is required by the system, then by filling in as much as he/she knows into the dialogue box, the system will output several data file names which are related to the information that the user has entered into the system. The user can then complete the choice from these files. On the other hand, if the user wants to add the data into the database, the system also displays a dialogue box which asks the user to enter the appropriate chemical information into it, the system then can decide the proper name and address for this particular file within the database.

IMPLEMENTATION OF RULES FOR ACdiagnosis

ACdiagnosis solves instrumental and chemical problems associated with flame atomic absorption analysis. We are using the expert system shell KDS-3 to develop our rule base. KDS-3 is an inductive expert system shell, that consists of a development component and a run time component. The development component allows information to be entered in the form of case histories broken into conditions and conclusions. The run time component permits distribution of the compiled version of the system to users. Because KDS-3 is an inductive expert system, the developer is required to specify knowledge in terms of conditions and conclusions. The relationship between each condition and conclusion is used to construct a set of rules. KDS-3 works in the sequence of facts...rules...knowledge base. This can be contrasted with subjective systems which evolve as rules...knowledge base. Facts are objective whereas explicitly entered rules are subjective since they consist of the opinions of one or more people. A computer with the proper software is far more capable of accurate and rapid logical analysis of a large number of facts than a human being.

The present module of ACdiagnosis is the second version of this expert system (4, 5). Here, we refer to the conditions as symptoms and the case conclusions as causes. We have determined the following symptoms:

1. Relative standard deviation values are high (>5%); absorbance values are not precise.
2. Absorbance values are 50-80% of the expected values in the calibration graph.
3. Absorbance values are 20-40% of the expected values in the calibration graph.
4. Noisy absorption signal (observed in signal graphics).
5. Occasional pulse up or down in signal (observed from signal graphics).
6. Signal decays during aspiration (observed from signal graphics).
7. Pulsating signal (observed from signal graphics).

8. The calibration graph levels off at high concentrations.
9. The calibration curve is sigmoidal.
10. Change in absorption sensitivity between re-calibration.
11. Drift in baseline.
12. The flame has a ragged appearance.
13. A refractory element is present in the solution.
14. The samples are viscous.
15. The uptake rate is less than 5ml/min.
16. Fluctuating display while optimizing lamp.
17. Hollow cathode lamp on but no display while optimizing lamp.
18. Spectrometer is in single beam mode.
19. Integration time is less than 3 seconds.
20. You are using an oxidizing flame.
21. Low pressure in the fuel cylinder.
22. The burner is set above 8 on the vertical scale.
23. You are using nitrous oxide-acetylene flame.

The symptoms may be broadly classified into (a) instrumental conditions that existed before the sample analysis took place, and (b) problems encountered during the sample analysis. Since KDS gives only one answer at a time which solves only one problem, the user is expected to take the suggested corrective action and then consult the expert system for a second time for further advice, if needed. KDS would work better in a completely automated system wherein the system would carry out the required corrective action and proceed with the analysis. For instance, if the cause of the problem is an unstable lamp, the system would change the lamp and perform lamp optimization before proceeding with the analysis. The feature of KDS which allows the user to choose the most important symptom from a screen displaying all the possible symptoms is very useful. It allows the user to give a response to symptoms in an order better related to the specific problem. Each reappearance of the volunteer screen excludes from its display the symptoms which have been resolved directly or through inference since its last appearance.

The problem in writing rule based expert systems in analytical chemistry is that the chemical information must be encoded into rules. The knowledge (facts and rules) in KDS is represented in the form of a matrix consisting of case conclusions or causes (rows) and conditions or symptoms (columns). The rules are generated by inductive analysis of all the facts in the module.

A rule of the form "if subject (true) then predicate (true)" is generated when both the symptoms (the subject and the predicate) could be caused by the same problem. The following rules were generated because the subject and the predicate of each rule are associated with the same cause.

Rule: If low pressure in the fuel cylinder (is true) then drift in baseline (is true).

Rule: If the flame has a ragged appearance (is true) then the relative standard deviation values will be high (>5%); absorbance values will not be precise (is true).

Rule: If low pressure in the fuel cylinder (is true) then noisy absorption signal will be observed in the signal graphics (is true).

A rule of the form "if subject (true) then predicate (false)" is generated when the subject and the predicate are not associated with the same problem, for example, "if relative standard deviation values are high (>5%); absorbance values will not be precise (is true) then the burner is set above 8 on the vertical scale (is false)". This means that when the burner blocks the optical path no signal would be seen.

We are now familiar with building diagnostic expert systems and have built one for troubleshooting in gas chromatography. We realize the importance of a friendly user interface and have started work on designing graphical images that will replace textual forms of symptoms.

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DP2

DEVELOPMENT OF A TURN-KEY SYSTEM FOR HAZARDOUS WASTES ANALYSIS

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SUMMARY

A turn-key hazardous wastes analysis system has been developed using Fourier transform attenuated total reflectance infrared spectrometry, artificial intelligence assisted library searching and an automated infrared interpreter. Both the library searching and the infrared interpreter take advantage of the portability, the computing power and the mass data storage available for PC systems and is demonstrated to be a cost effective tool to assure consistent data interpretation. This turn-key system has a 10 nanogram detection limit and provides fast sample turn-around-time. The possibility of direct sample analysis without any clean-up process is demonstrated. Preliminary results from this developmental work indicate the possible improvement of sample throughput by as much as 300%.

INTRODUCTION

This automated infrared interpreter was developed on an IBM personal computer (PC) running under the Microsoft disk operating system (DOS). Based on the original Merck Sharp & Dhome Research Laboratory Program for the Analysis of Infrared Spectra (PAIRS) (1,2), this infrared interpreter, PC PAIRS⁺, is capable of analyzing infrared spectra measured with a wide variety of spectrophotometers. Modifications have been made to PAIRS to enable the application of both artificial intelligence and library searching. Furthermore, a new algorithm has been devised to combine the results from the library searching and the PAIRS program to obtain high confidence level interpretational data. Major functionalities of the PC PAIRS$^+$ are illustrated in Figure 1.

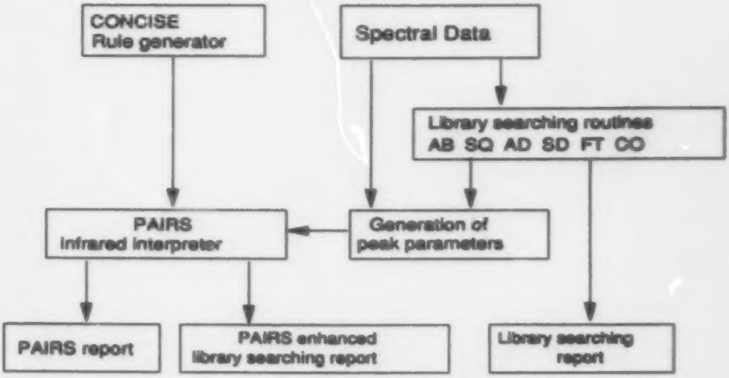
CONCISE
Rule generator
Spectral Data
Library searching routines
AB SQ AD SD FT CO
PAIRS
Infrared Interpreter
Generation of
peak parameters
PAIRS report
PAIRS enhanced
library searching report
Library searching
report

Figure 1. Functionalities of PC PAIRS+

All software was developed on a Magus Data Technology (Richmond Hill, Onatrio) 80386/80387 IBM DOS PC running at a clock speed of 20 MHz. The original PAIRS and the infrared interpretation rule generator, the Computer Oriented Notation Concerning Infrared Spectral Evaluation (CONCISE) (3,4) language, were obtained from the Quantum Chemistry Program Exchange (Bloomington, Indiana, Catalog # QCPE 426). The programs were downloaded into the PC via a RS-232 line from a VAX 780 system. Both programs were modified and converted to standard Ryan McFarland FORTRAN (Phoenic Computer Products, Norwood, MA) conventions, compiled and run on the same PC.

The library searching subprogram used five search algorithms. They are: absolute difference (AB), square of absolute difference (SQ), absolute difference of first derivative (AD), square of difference of first derivative (SD) and time domain cross correlation (FT). One additional algorithm was developed as part of this project to combine the library searching results from the first five algorithms, the combined algorithm (CO).

EXPERIMENTAL

A. Chemicals and Method of Analysis. A total of 67 oil and grease samples were measured in this work. These samples are standards of the most commonly encountered petroleum hydrocarbons and greases in the province of Ontario. A Barnes (SpectraTech Inc., Stamford, CT) micro circle cell accessory was used to measure the attenuated total reflectance (ATR) spectra of the samples. These spectra then formed the MOE Oil & Grease Library.

Several ATR infrared spectra were generated to test the software and the Oil & Grease library. Typically, about 2 ml of oil samples were used to spike one litre of tap water. Using the standard MOE method for the solvent extractable (5) the oils was extracted from the water sample using dichloromethane. Upon evaporation of the solvent the infrared spectrum of the residue was measured

B. Instrumentation. Either a BOMEM MB-100 (Quebec, Quebec) or a Nicolet 5SX (Madison, WI) Fourier transform infrared (FT-IR) spectrometer was used to measure the spectra. An optical retardation of 0.25 cm was used to signal average 100 single sided interferograms with a resolution of 2 cm^{-1}. The BOMEM FT-IR used an IBM DOS PC computer for the data collection and manipulation. For the Nicolet 5SX FT-IR, a Nicolet 620 data system was used to serve the purposes. Spectra measured with the BOMEM FT-IR were used without any change. For spectra measured on the Nicolet FT-IR a NICOMPC communication software (Nicolet Inc., Madison, WI) was used to download the spectra into the PC via a RS-232 line. The downloaded spectra were then used to create the spectral library.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the process employed by PC PAIRS$^+$ in the evaluation of unknown spectra and report generation. Library searching was used for the positive identification of unknowns. In order to minimize the effect of noise and baseline problems of the infrared spectrum, results from all five library searching algorithms (AB, SQ, AD, SD, CO) were combined to determine the best match for the unknown. Table 1 illustrates a typical library searching report from this turn-key system. The test sample used was IOSOL 1520, a common paint thinner used for the oil based paint. The library searching routine was set to list the five best matches from each individual routine. From Table 1, the AB and the SQ algorithms fail to identify the unknown from the Oil & Grease library. The CO method, on the other hand, successfully identified this unknown and many others, supporting its use as the method of choice for the library searching.

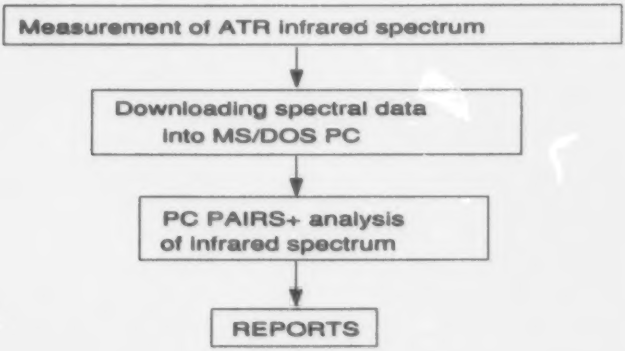
Measurement of ATR infrared spectrum
Downloading spectral data into MS/DOS PC
PC PAIRS+ analysis of infrared spectrum
REPORTS

Figure 2. Procedures for a typical unknown sample analysis using the turn-key system.

Although the oil library with the five search algorithms have been successful for the identification of many routine sample analysis, we have encountered some situations where PAIRS⁺ proved to be superior. To illustrate this we added digital noise to a spectrum of Turbo A-1 oil to simulate the spectrum of an unknown organic extracted with dichloromethane. This spectrum was then searched through our oil library using CO algorithm. The result is shown in Figure 3. From this Figure, it is clear that all three matches and the test spectrum have identical spectra which makes the identification of the test spectrum from the library searching results impossible. Using PAIRS⁺, although interpretational results from the infrared interpreter indicated the presence of methyl and methylene group in the unknown and in all three matches, the probability order for the " functional groups" identifies the match #1 as the correct identification. These results are listed in Table 2. By comparing the probabilities obtained for match #1 with those obtained for matches #2 and #3 one can conclude that only match #1 is the correct answer.

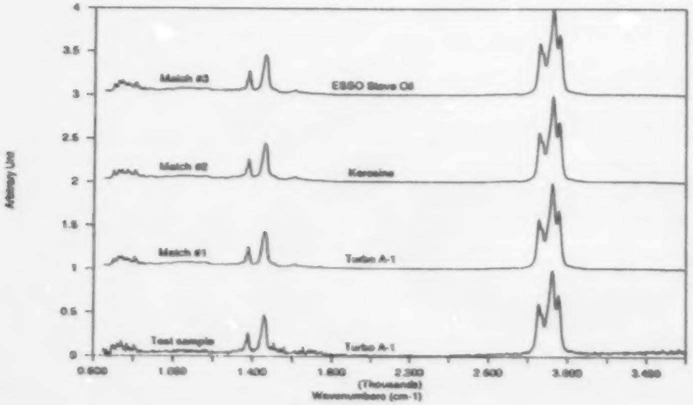

Figure 3. Library searching results for the test sample using the CO method. The close resemblance between the unknown and the three matching spectra complicates the task of positive identification requiring.

CONCLUSIONS

A turn-key system has been developed to utilize artificial intelligence and the positive identification capability of the library searching. The CO algorithm which combines results from five different library searching routines can obtain high quality library searching data. The typical analysis time of this turn-key system, including the data entry, the library searching and the final PAIRS' interpretation, is about five minutes per sample. PC PAIRS$^+$ not only increases the sample throughput of routine sample identification in the laboratory but also standardizes the procedure of infrared data interpretation. Current system is with an enhanced user interface and takes advantage of the ready access and user friendly nature of PC computer systems, therefore, can be an invaluable training system in the laboratory.

REFERENCES

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2. Woodruff, H.B. and Smith, G.M., Anal. Chem., 52, 2321 (1980).
3. Woodruff, H.B. and Smith, G.M., Analytica Chimica Acta, 133, 545 (1981).
4. Tomellini, S.A., Hartwick, R.A., Stevenson, J.M. and Woodruff, H.B., Analytica Chimica Acta, 162, 227 (1984).
5. Ontario Ministry of the Environment Method SXT-E3201A.1, Rexdale, Ontario, Canada.

Table 1. Typical PC PAIRS+ Library Searching Report

```
  The sample spectrum is: IOSOL 1520
    The reference library is: >>>>>  The Oil Library <<<<<
              The Library Search Result
              ==============================
                ( The FT Method )
* Match #1 with probability of >>>>>>>>     0.020430  <<<<<<<<
      File #  35: IOSOL 1520, TRACE ORGANICS
* Match #2 with probability of >>>>>>>>     0.024283  <<<<<<<<
      File #  19: ESSO REGULAR GASOLINE, TRACE ORGANICS
* Match #3 with probability of >>>>>>>>     0.026579  <<<<<<<<
      File #  21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>>>>     0.029905  <<<<<<<<
      File #  32: ISOPAR'K', TRACE ORGANICS
* Match #5 with probability of >>>>>>>>     0.052817  <<<<<<<<
      File #   4: DISTILLED ISOPAR H, TRACE ORGANICS
              The Library Search Result
              ==============================
                ( The AB Method )
* Match #1 with probability of >>>>>>>>    27.904972  <<<<<<<<
      File #  16: IOSOL 1125, TRACE ORGANICS
* Match #2 with probability of >>>>>>>>    30.336798  <<<<<<<<
      File #  32: ISOPAR'K', TRACE ORGANICS
* Match #3 with probability of >>>>>>>>    30.400099  <<<<<<<<
      File #  21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>>>>    32.325081  <<<<<<<<
      File #  53: TURBO FUEL, TRACE ORGANICS
* Match #5 with probability of >>>>>>>>    32.441692  <<<<<<<<
      File #  27: IOSOL 2024, TRACE ORGANICS
              The Library Search Result
              ==============================
                ( The AD Method )
* Match #1 with probability of >>>>>>>>     2.182141  <<<<<<<<
      File #  35: IOSOL 1520, TRACE ORGANICS
* Match #2 with probability of >>>>>>>>     3.216939  <<<<<<<<
      File #  32: ISOPAR'K', TRACE ORGANICS
* Match #3 with probability of >>>>>>>>     3.284418  <<<<<<<<
      File #  21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>>>>     4.126999  <<<<<<<<
      File #  16: IOSOL 1125, TRACE ORGANICS
* Match #5 with probability of >>>>>>>>     4.243579  <<<<<<<<
      File #  24: VARSOL 3135, TRACE ORGANICS
              The Library Search Result
              ==============================
                ( The SD Method )
```

```
* Match #1 with probability of >>>>>>>>       0.010901  <<<<<<<<:
      File #  35: IOSOL 1520, TRACE ORGANICS
* Match #2 with probability of >>>>>>>>       0.045700  <<<<<<<<:
      File #  32: ISOPAR'K', TRACE ORGANICS
* Match #3 with probability of >>>>>>>>       0.047074  <<<<<<<<:
      File #  21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>>>>       0.072051  <<<<<<<<:
      File #  34: TETRAMER 'M', TRACE ORGANICS
* Match #5 with probability of >>>>>>>>       0.072871  <<<<<<<<:
      File #  16: IOSOL 1125, TRACE ORGANICS

            The Library Search Result
            ==========================
              (  The SQ Method  )

* Match #1 with probability of >>>>>>>>       0.935763  <<<<<<<<:
      File #  32: ISOPAR'K', TRACE ORGANICS
* Match #2 with probability of >>>>>>>>       0.974765  <<<<<<<<:
      File #  21: ISOPAR 'M', TRACE ORGANICS
* Match #3 with probability of >>>>>>>>       1.086680  <<<<<<<<:
      File #  35: IOSOL 1520, TRACE ORGANICS
* Match #4 with probability of >>>>>>>>       1.636677  <<<<<<<<:
      File #   4: DISTILLED ISOPAR H, TRACE ORGANICS
* Match #5 with probability of >>>>>>>>       1.791006  <<<<<<<<:
      File #  16: IOSOL 1125, TRACE ORGANICS

            The Library Search Result
            ==========================
             (The Combined Method)

* Match #1 with probability of >>>>>>>>     145.076797  <<<<<<<<:
      File #  35: IOSOL 1520, TRACE ORGANICS
* Match #2 with probability of >>>>>>>>     248.866852  <<<<<<<<:
      File #  32: ISOPAR'K', TRACE ORGANICS
* Match #3 with probability of >>>>>>>>     249.893478  <<<<<<<<:
      File #  21: ISOPAR 'M', TRACE ORGANICS
* Match #4 with probability of >>>>>>>>     404.149170  <<<<<<<<:
      File #  16: IOSOL 1125, TRACE ORGANICS
* Match #5 with probability of >>>>>>>>     444.879761  <<<<<<<<:
      File #  53: TURBO FUEL, TRACE ORGANICS

                          The Library Search Summary
                          ===========================

                                          Library ID
Method              Hit # 1      Hit # 2      Hit # 3      Hit # 4      Hit # 5
-------------------------------------------------------------

1.   AB               16           32           21           53           27
2.   AD               35           32           21           16           24
3.   SD               35           32           21           34           16
4.   SQ               32           21           35            4           16
5.   FT               35           19           21           32            4
6.   CO               35           32           21           16           53
```

Table 2. Typical report from the automated infrared interpreter

```
Spectral data summary for:  Turbo A-1
The solvent is: neat
No empirical formula given

 There are          8 peaks
 Line      Width        Intensity   Location
    1      sharp        3              727
    2      average      1             1367
    3      sharp        3             1379
    4      average      4             1460
    5      sharp        4             1464
    6      average      5             2873
    7      average      8             2925
    8      average      10            2956
Printout is sorted by probability:

    Group name                      Probability
    1) METHYL                           0.85
    2) METHYLENE                        0.49
    3) AROMATIC                         0.05
    4) ACID                             0.05
    5) HETEROAROMATIC                   0.01
    6) PYRIDYL                          0.01
    7) PYRAZYL                          0.01
    8) PYRIMIDYL                        0.01
    9) PURINE                           0.01
    10) INDOLE                          0.01
Interpretation for library match # 1......

Spectral data summary for: Turbo A-1, TRACE ORGANICS
The solvent is: neat
No empirical formula given

 There are          7 peaks
 Line      Width    Intensity        Location
    1      average      2              727
    2      average      2             1377
    3      average      4             1456
    4      average      5             2856
    5      sharp        6             2870
    6      average      10            2922
    7      sharp        9             2952
Printout is sorted by probability:

    Group name                      Probability
    1) METHYLENE                        0.71
    2) METHYL                           0.60
    3) ACID                             0.05
    4) PYRROLE                          0.00
    5) FURAN                            0.00
    6) THIOPHENE                        0.00
    7) AROMATIC                 0.00
    8) AROM-MONOSUBST           0.00
    9) Z1                       0.00
    10) AROM-1.2-SUBST          0.00

Interpretation for library match # 2......

Spectral data summary for: Kerosine, TRACE ORGANICS
The solvent is: neat
No empirical formula given

There are          24 peaks
 Line     Width    Intensity        Location
    1     sharp        1              729
    2     sharp        1              739
    3     sharp        1              771
    4     sharp        1              918
    5     sharp        1              964
    6     sharp        1              980
    7     sharp        1              1007
    8     sharp        1              1043
    9     sharp        1              1055
   10     sharp        1              1063
   11     sharp        1              1066
   12     sharp        1              1074
   13     sharp        1              1090
   14     sharp        1              1097
   15     sharp        1              1124
   16     sharp        1              1151
   17     sharp        1              1169
   18     sharp        1              1340
   19     sharp        3              1365
   20     average      4              1379
   21     average      5              1464
   22     average      6              2873
   23     broad        7              2927
   24     average      10             2956
 Printout is sorted by probability:

    Group name                    Probability
    1) METHYL                        0.88
    2) ACID                          0.75
    3) METHYL-GEMDI                  0.55
    4) KETAL                         0.45
    5) AMINE                         0.40
    6) AMINE-TERTIARY                0.40
    7) ACETAL                        0.40
    8) NH3+                          0.25
    9) MERCAPTAN                     0.25
    10) METHYLENE                    0.22
    11) AROMATIC                     0.05
    12) HETEROAROMATIC               0.01
    13) PYRIDYL                      0.01
    14) PYRAZYL                      0.01
    15) PYRIMIDYL              0.01
    16) PURINE                 0.01
    17) INDOLE                 0.01
    18) PYRROLE                0.00
    19) FURAN                  0.00
    20) THIOPHENE              0.00

Interpretation for library match # 3.....

Spectral data summary for: ESSO Stove Oil, TRACE ORGANICS
The solvent is: neat
No empirical formula given

There are    22 peaks
 Line     Width    Intensity      Location
    1    average       1             739
    2    sharp         1             773
    3    sharp         1             918
    4    sharp         1             964
    5    sharp         1            1007
    6    sharp         1            1032
    7    sharp         1            1038
    8    sharp         1            1045
    9    sharp         1            1055
   10    sharp         1            1059
   11    sharp         1            1068
   12    sharp         1            1082
   13    sharp         1            1103
   14    sharp         1            1122
   15    sharp         1            1151
   16    sharp         1            1169
   17    sharp         3            1365
   18    average       4            1379
   19    average       5            1460
   20    average       6            2871
   21    sharp         7            2927
   22    average      10            2956

Printout is sorted by probability:

    Group name              Probability
    1) METHYL                  0.93
    2) ACETAL                  0.84
    3) METHYL-GEMDI            0.55
    4) KETAL                   0.52
    5) METHYLENE               0.49
    6) AMINE                   0.40
    7) AMINE-TERTIARY          0.40
    8) AROMATIC                0.05
    9) ACID                    0.05
    10) HETEROAROMATIC         0.01
    11) PYRIDYL                0.01
    12) PYRAZYL                0.01
    13) PYRIMIDYL              0.01
    14) PURINE                 0.01
    15) INDOLE                 0.01
```

Study of the Effect of Solvent and Stationary Phase on the Chromatographic Behaviour of PAHs

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Chemistry Department, Brock University,
St. Catharines, Ontario L2S 3A1

Preliminary observation has shown that peak shapes of PAHs on capillary GC/MS were influenced by the initial temperature used[1]. Fronting was observed in several early-eluting peaks of 16 priority PAHs in toluene when the initial temperature was lower than 110 °C. When the initial temperature was higher than 130 °C, peak tailing occurred. To find more detailed information, the effect of initial temperature on peak shape was further investigated and proved to be more severe when initial temperature is very low. The chromatographic behaviour of PAHs on GC was found to be strongly influenced by the properties of the solvent used for injection and the stationary phase. An explanation is suggested based on these observations. Interactions between various factors, such as initial temperature, injection volume, solvent, and stationary were also studied. Since previous results suggests that better sensitivities of PAHs can be obtained with a high boiling point solvent, a wide range of solvents with boiling points from 40 °C for dichloromethane to 151 °C for nonane and even to 215 °C for dodecane. The best response was found with nonane as solvent.

Effect of initial temperature on peak shape

A series of experiments were performed with the initial temperature varied from 88 °C to 258 °C. GC/MS peak profiles were obtained when a 2 µl solution of 2 µg ml^{-1} of each PAH in p-xylene was injected at an initial temperature of (a) 88 °C, (b) 128 °C, and (c) 138 °C. Peak shape varies significantly with the initial column temperature. When the initial temperature is 138 °C, a chromatogram with symmetric GC peaks is obtained . However,with the decrease of the initial temperature, the effect of fronting and splitting of the PAH peaks became greater. Fronting of the GC peaks appears at the initial column temperature of 128 °C and each peak is split into two when the initial temperature was 88 °C. Similar effects were observed when PAHs were made up in other aromatic solvents, such as benzene and toluene. This splitting phenomenon was mainly observed for the first 10 peaks of the 16 PAHs.

In order further to study the dependence of peak profiles on initial temperature, a number of experiments were carried out under different initial temperatures, while other parameters were kept constant. Peak shapes of each of 16 PAHs in different solvents were recorded at different initial temperatures. The relation between peak shape of each PAH and initial temperature is illustrated in Figures 1-4. Figures 1, 2, 3, and 4 were obtained when toluene, p-xylene, isooctane and nonane were used as solvents. The boiling points on the X axis correspond to each PAH determined. Peaks except 13, 15 and 16 are presented in these figures. The upper curve in Figures 1-4 shows the maximum initial temperatures, above which peaks start tailing. The lower curve shows the minimum initial temperature, below which fronting of peaks is observed. These two curves divide the space into three regions. Within the bottom region, under the minimum initial temperature curve, fronting or split peaks occurred. Tailing peaks were observed in the top region above the maximum initial temperature curve. In the middle region, between the two curves, very good symmetrical peaks were obtained, indicating the optimum initial temperature with regard to peak shape. As shown in the Figures, the optimum initial temperature varies with different PAHs. This optimum range generally increases with the increase of boiling points of PAHs. Thus the early eluting PAH peaks have narrow critical ranges, whereas the late eluting PAHs give much wider optimum range. Below the minimum initial temperature curve, GC peaks begin to exhibit fronting and the fronting or splitting of peaks worsens as the temperature decreases. Similarly, tailing of the peak gradually occurs above the maximum initial temperature shown in the Figures, and becomes more severe when the initial temperature increases more over the maximum initial temperature.

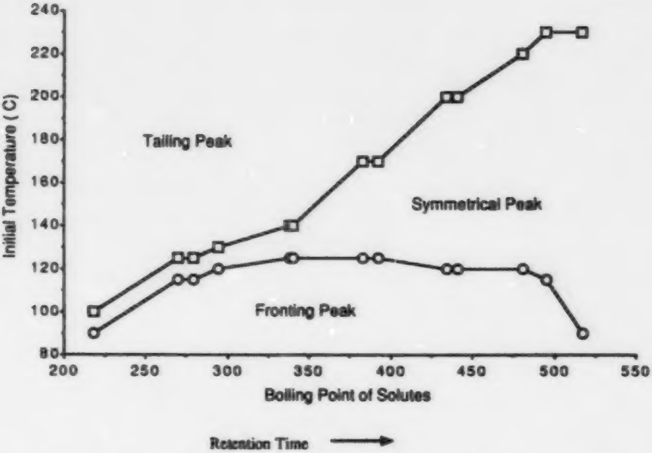

Figure 1. Effect of Initial Temperature on Peak Shape of 16 PAHs in Toluene

Conditions: temperature program one; crosslinked methyl silicone column; injection volume: 2 μl of 2 μg ml^{-1} PAHs in toluene.

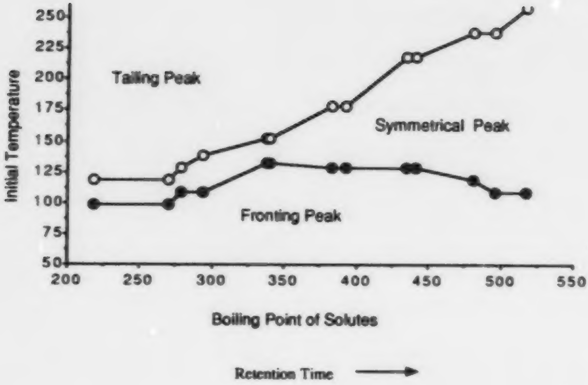

Figure 2. Effect of Initial Temperature on Peak Shape of 16 PAHs in p-Xylene

Conditions: temperature program two; others see Figure 1.

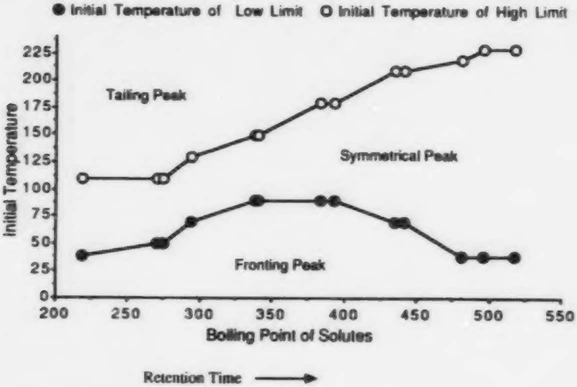

Figure 3. Effect of Initial Temperature on Peak Shape of 16 PAHs in Isooctane

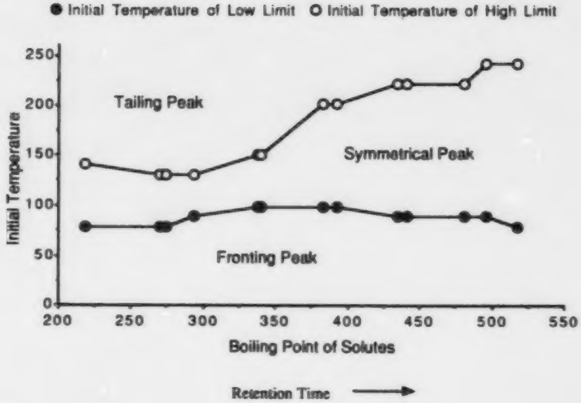

Figure 4. Effect of Initial Temperature on Peak Shape of 16 PAHs in Nonane

The optimum initial temperature range also depends on the solvent used for the injection of PAHs. Comparing figure 1-4, we can see that the ranges of initial temperature for symmetrical peaks are larger in alkane solvents such as isooctane and nonane than that in aromatic solvents like toluene and p-xylene. The optimum ranges of initial temperature for symmetrical peaks 2 and 3, for example, are approximately 110 to 120 °C in toluene, 108 to 138 °C in p-xylene, 49 to 109 °C in isooctane, and 81 to 141 °C in nonane as illustrated in the above figures.

Reference:

1. Ian D. Brindle and Xing-fang Li, Journal of Chromatography, 1990, 498, 11-24.

DP4

MONITORING AMBIENT AIR VOCs USING CRYOGENIC AND ADSORBENT TRAP

A CRITICAL EVALUATION

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INTRODUCTION

Analysis of ambient air volatile organic compounds (VOCs) is a complex task. This is due primarily to: 1. the wide variety of compounds of interest and 2. an ineffective means of analysis. The US EPA suggested a core set of three methods for sampling and analysis of ambient air VOCs (1). For the complete analysis of VOCs having boiling points from -10 to 200oC, the method suggested the use of a cryogenic analytical trap. This has been the method of choice, because it allows for the complete analysis of VOCs in a once-through type of operation. Of course, the use of a liquid N_2 cooled trap would imply the limited mobility of the system. This cryogenic trap also implies that atmospheric water vapor would be frozen in the trap, thus, clogging the trap and finally be desorbed into the GC. Therefore, creating many retention indices shift problems during the separation. In addition, with the equipment being operated at two extreme of temperatures, i.e., from - 196 to 220°C, it would always be a major contributing factor to the downtime.

One alternative to the cryogenic analytical trap is an adsorbent packed analytical trap. The advent of a new variety of adsorbents grants us the capability of adsorbing/desorbing compounds with a fairly wide range of boiling points. We have therefore evaluated in this work, the validity of using an adsorbent analytical trap to do the analysis on the VOCs. Presented in this paper is the description of the objectives and results obtained from this work. Preliminary results were obtained using two adsorbent packed analytical traps. QA/QC data will be presented to demonstrate the advantages/disadvantages of using an adsorbent analytical trap for the VOC analysis.

EXPERIMENT

The adsorbent based analytical trap VOC thermal desorption / gas chromatograph / mass spectrometer system (TD/GC/MS) consists of a Tekmar LSC2000 thermodesorber (Cincinnati, OH), a Tekmar 4210 autosampler, a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and a Hewlett-Packard 300 series data station. The cryogenic trap VOC TD/GC/MS system consists of a Tekmar 5010 thermodesorber (Cincinnati, OH), a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and an Intel 80386/80387 based data station. Figure 1 illustrates a general block diagram of the two systems.

Two adsorbent analytical traps were used to concentrate the VOCs for the subsequent GC/MS analysis. Both analytical traps were obtained from Supelco Canada (Oakville, Ontario). The first one is a standard adsorbent trap (Supelco Cata. # 2-0321). The second analytical trap is a proprietary trap (2), courtesy of

Supelco Canada. Spiking mixtures were prepared using a modified gas mixing chamber (Lasale Glass, Barrie, Ontario). All data presented was obtained from both within run and between run experiments.

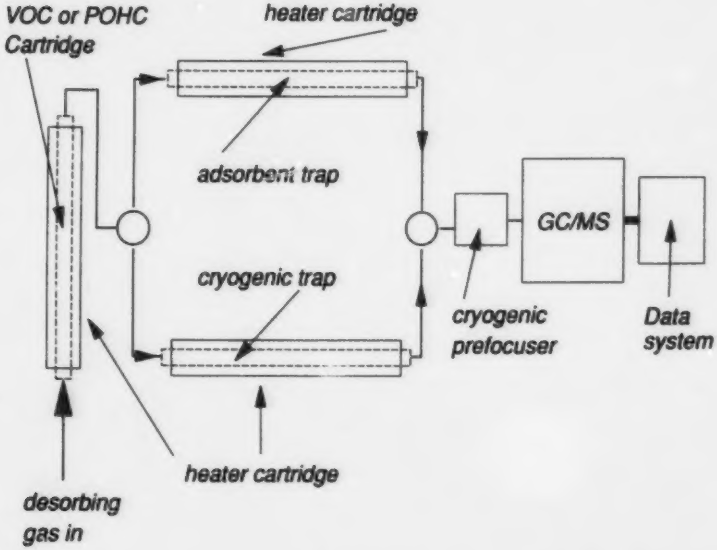

VOC or POHC Cartridge
heater cartridge
adsorbent trap
GC/MS
cryogenic trap
cryogenic prefocuser
Data system
heater cartridge
desorbing gas in

Figure 1. Block diagram of cryogenic and adsorbent based TD/GC/MS systems for the ambient air VOC analysis.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the total ion chromatogram (TIC) obtained from the cryogenic TD/GC/MS system. Figure 3 illustrates the TIC obtained from the adsorbent based TD/GC/MS system. Table 1 illustrates the QA/QC evaluation data obtained from the proprietary adsorbent trap TD/GC/MS system. Standard deviation data obtained from the standard adsorbent trap was too high to be useful. Table 2 illustrates prelimarily QA/QC data obtained from the cryogenic analytical trap TD/GC/MS system.

It is peculiar to note that we could not obtain useful data from the standard trap (Supelco cata.# 2-0321) which was capable of trapping the low boiling point volatile organic compounds under the purge and trap GC operation. The new trap (2) would allow us to trap the low boiling point VOCs in the TD/GC/MS system. Future studies are required to address this question.

CONCLUSION

We have demonstrated that applying adsorbent based TD/GC/MS system for the ambient air VOC analysis is feasible. Possibility of eliminate a cryogenic trap for the TD/GC/MS system offers a cost effective approach for the VOC analysis. Problems from liquid nitrogen related instrument downtime would have been eliminated, achieving a constant, maximized sample throughput.

REFERENCES

1. "Compendium of methods for the determination of toxic organic compounds in ambient air", R.M.Riggin, Battelle-Columbus Laboratories, Columbus, Ohio.
2. Robert Belardi, Supelco Canada, Oakville, Ontario, private communication.

TABLE 1. QA/QC DATA OBTAINED FROM AN ADSORBENT ANALYTICAL TRAP TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*	
		within	between
METHYL CHLORIDE (-23)	103.3	21.4	34.61
VINYL CHLORIDE (-13.9)	136.8	16.22	43.40
1,3-BUTADIENE (-4.5)	97.5	17.41	47.72
1,1-DICHLOROETHANE (31.9)	182.7	19.02	43.98
TRICHLOROMETHANE (61)	222.6	29.3	32.83
BENZENE (80)	131.8	33.03	42.78
BROMODICHLOROMETHANE (90)	295.65	31.07	43.04
TOLUENE (110)	129.9	23.62	34.11
1,2-DIBROMOMETHANE (131)	405.11	30.48	47.12
CHLOROBENZENE (131)	166.11	21.05	36.55
1,2-DICHLOROBENZENE (180)	195.0	9.48	18.48
NAPTHALENE (217)	174.3	16.61	14.57

* Presented in ±% to the spiked amount. The within run and between run data was obtained from 11 and 23 experiments, respectively.

TABLE 2. QA/QC DATA OBTAINED FROM AN CRYOGENIC ANALYTICAL TRAP TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*
METHYL CHLORIDE (-23)	103.3	N/A
VINYL CHLORIDE (-13.9)	136.8	N/A
1,3-BUTADIENE (-4.5)	97.5	11.32
1,1-DICHLOROETHANE (31.9)	182.7	8.80
TRICHLOROMETHANE (61)	222.6	9.41
BENZENE (80)	131.8	10.2
BROMODICHLOROMETHANE (90)	295.7	18.9
TOLUENE (110)	129.9	6.73
1,2-DIBROMOMETHANE (131)	405.2	N/A
CHLOROBENZENE (131)	166.1	4.39
1,2-DICHLOROBENZENE (180)	195.0	4.81
NAPTHALENE (217)	174.3	8.23

* Presented in ±% to the spiked amount. Data obtained from 8 within run experiemnt.

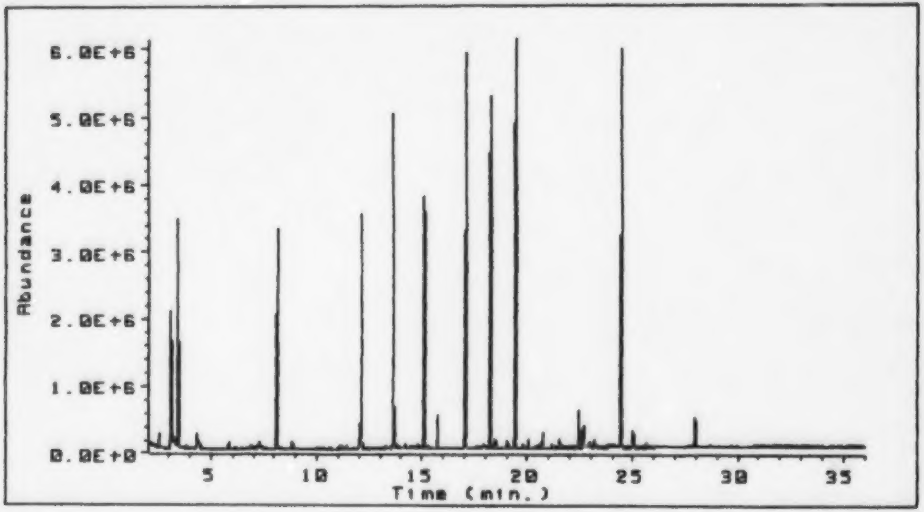
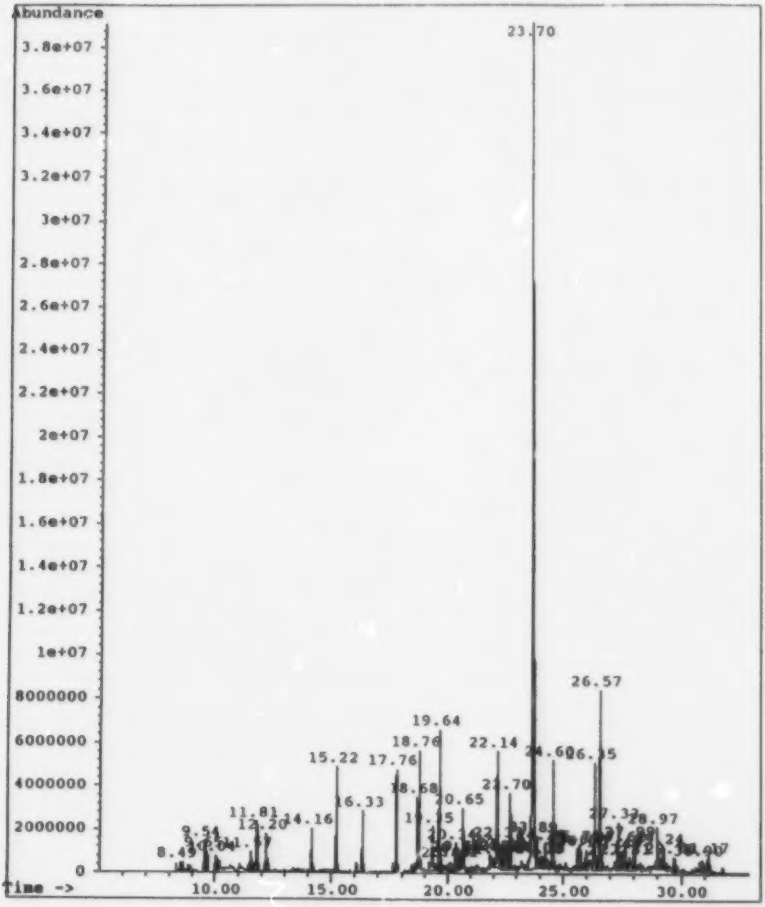


Figure 2: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system.

Figure 3: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system using Cryogenic Analytical Trap.



ADAPTATION OF WATER PRECONCENTRATION TECHNIQUES DEVELOPED FOR PCDD ANALYSIS TO OTHER TARGET ORGANIC POLLUTANTS.

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INTRODUCTION

These laboratories, in conjunction with the Ontario Ministry of Environment, have developed a sampling unit capable of preconcentrating water for ultratrace detection of PCDDs as part of a water quality monitoring program for raw and treated drinking water[1].

The automatic preconcentration sampler (APS) incorporates both filtration and adsorption technology. The adsorption technology utilizes a macroreticular resin (XAD-2) column, in duplicate, for which sampling conditions and elution and detection procedures have been established to permit recovery and analysis of dioxins at the ppq level[2]. The filter system is based on setting the distinction between dissolved and insoluble particles at 0.45 um. The duplicate filter systems each consist of 2 tubular filters placed in series to accommodate approximately 30 L of 5-10 NTU water and trapping >0.3 um particles at 98% retention.

It is essential to incorporate filtration in a sampling unit since natural water contains suspended mineral particles, coated with colloidal metal oxides and humic acids, which adsorb and transport significant amounts of organic contaminants. In conventional water sampling techniques, using only adsorption media, the presence of particulate matter interferes with the accurate recovery and quantitation of the analytes. The APS overcomes this loss factor by preconcentrating organics using analytical filtration and resin technology in series.

Calibration experiments to determine dioxin recoveries using the APS showed that all dioxin congeners tested were located on the filter, with no detectable levels on the XAD-2 resin[1]. Other laboratories, when analyzing river water for PCBs, have found that a substantial portion of the organochlorines from the water sample was located on the filtered sediment(3,4). Thus, in its present configuration, the APS can be adapted to the detection of two types of organic contaminants; those which are adsorbed on particulates and retained by the filter, and those which remain dissolved in the aqueous phase and adsorbed on the XAD column.

In order to develop a more comprehensive protocol for the APS unit, the behaviour of eight compounds selected from the Ontario Ministry of the Environment priority pollutant list have been studied in the presence of a representative clay suspension.

EXPERIMENTAL

The compounds chosen for this study include two polyaromatic hydrocarbons, benzoperylene and anthracene, and five organochlorines, PCBs, 1,2,4-trichlorobenzene, octachlorostyrene, 2,4,5-trichlorotoluene, lindane and Mirex. These compounds vary in aromaticity, molecular weight, and degree of chlorination since these characteristics may influence the distribution behaviour.

APS Testing

The first run consisted of 40 L of distilled water only, passed through filters and columns, to observe background noise. The remaining experiments were performed using a 40 L spike solution of the target organics in distilled/deionized water, pumped at flow rate of 200 mL/min and a concentration of 10 ng/L, through the sampler (a total of 400 ng of each target compound was passed through the sampler). One run involved passing the spike solution through the column only so it could be evaluated without the interference of the filters. The behaviour of target organics was then studied as a function of turbidity. Illite solutions at turbidities of 0, 0.1, 0.5, 1, 5 and 10 NTU were passed through the filters and columns.

In situ Extraction Apparatus

The current procedure for extraction of organic analytes from a solid matrix such as a filter or soil sample is soxhlet extraction.

To adapt this process to Balston or cartridge filters there are several problems. To accommodate the filter size, a soxhlet apparatus must have a sample chamber of 1500 mL or 5000 mL which can cost $700.00 or $1200.00 respectively. An apparatus of this size is awkward to clean and handle on a routine basis.

In addition, in order to use a traditional Soxhlet apparatus, the filter must be transferred from the filter housing to the apparatus without compromising the analytical integrity of the filter or contaminating the worker by exposure to toxic chemicals on the filter.

The objective of this part of the study was to examine the feasibility of an *in situ* Soxhlet extractor using the filter housing as the sampler compartment of the extraction vessel.

A prototype has been constructed. The main feature consists of a glass adapter which connects the condenser to the round bottom flask. This adapter contains the syphon and a small built-in funnel that is designed to collect the condensed solvent and carry it to the filter housing. The glass tube extending from this funnel is connected to a flexible stainless steel tube which ends in a Swagelok connector used to join the assembly to the filter housing. Through this connection the solvent enters the housing. The solvent exits at the bottom of the housing through an identical connection. After the stainless steel tube joins the glass tube, the glass makes a ninety degree turn upwards to form the syphon.

There was no time in the study to test this apparatus for efficiency of extraction.

RESULTS AND DISCUSSION

Method tests of filter extraction and extract preparation for instrument analysis were performed on all spike compounds to determine efficiency of the procedure for recovery of analytes. The values are shown in table 1. Column extraction recoveries were not evaluated in this study since they have been done in other work[5].

The most volatile of the compounds, 1,2,4-trichlorobenzene, was not recovered well, probably due to evaporative losses. Moderately volatile compounds such as 2,4,5-trichlorotoluene and anthracene also showed some evaporation loss. Benzoperylene was not recovered at all probably because this heavy compound remained on the glassware during the work up stage. It would appear as though the recovery of analytes from the filters suffered similar losses as the sample work up, meaning that the compounds were extracted reasonably efficiently from the filter. However, additional losses will occur with volatile compounds because of the nature of soxhlet extraction.

Interferences were evaluated in the filters and column and the results are shown in table 2. Lindane, anthracene and PCBs were found in the column, AAQ filter and BQ filters. Obviously, these interferences vary from filter to filter since the AAQ filter was severely contaminated.

Also evaluated was the glass spike carboy used to introduce compounds to the sampler, to observe loss of the analytes at this stage. The most heavily chlorinated compounds, Mirex and PCBs were found in relatively high concentrations in all three washes. Trace amounts of 2,4,5 - trichlorotoluene, lindane and anthracene were also observed in the wash samples.

Table 3 shows the results from the APS testing. No trend was observed in distribution of organic pollutants as a function of turbidity. Those compounds which were found predominately on the filters; octachlorostyrene and mirex; were present even when no particles were added. This would indicate that the compounds are attracted to the glass fiber in the filters.

Interferences were observed in both the columns and the filters although the contamination in the filters was much more severe. It is possible that there were two sources of contamination. The filters showed very high background levels of chlorinated hydrocarbons (PCBs, lindane, anthracene and sometimes 2,4,5 - trichlorotoluene) which would indicate that these compounds are used or produced in the manufacture of the filters. It is uncertain where the interferences from the columns were coming from (a dirty fume hood where samples were prepared is one speculation).

Because of the degree of PCB, lindane and anthracene contamination in the filters and columns it is difficult to observe any distribution pattern. Trichlorobenzene was the only compound found exclusively on the columns. The amount recovered represents approximately 14% of the original amount, which corresponds with the method test recovery value. Trichlorotoluene was found mostly on the column, except when the filters showed contamination of this compound. Mirex and octachlorostyrene were found exclusively on the filters.

TABLE 1

Compound	**Percent Recovery** Sample Workup Only	 AAQ Filter	 BQ Filter
1,2,4-trichlorobenzene	14	7	0
2,4,5-trichlorotoluene	81	46	3
Lindane	88	164	96
Anthracene	56	104	20
Octachlorostyrene	35	245	56
Mirex	248	170	71
Benzoperylene	0	0	0
PCBs	121	146	99

TABLE 2

AMOUNT RECOVERED FROM BLANK & WASH SAMPLES

Amount of each compound (ng)

Sample	TCB	TCT	Lin	Ant	Oct	Mir	Ben	PCB
Column Blank	---	---	60	5	---	---	---	202
BQ-Blank #1	---	---	68	10	---	---	---	244
BQ-Blank #2	---	---	227	31	---	---	---	138
AAQ-Blank	---	---	65950	1580400	---	---	---	547
Wash #1	---	---	35	8	---	32	---	234
Wash #2	---	16	38	6	---	329	---	269
Wash #3	---	18	50	4	---	316	---	248

TABLE 3

Run#	Illite NTU	Spike	TCB(ng)		TCT(ng)		LIN(ng)		ANT(ng)		OCT(ng)		MIR(ng)		BEN(ng)		PCB	
			C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F
1	0	N	---	---	---	---	187	1548	87	176	---	---	---	---	---	---	150	4513
2	0	Y	63	NA	508	NA	133	NA	696	NA	0.2	NA	59	NA	---	---	217	NA
3	0	Y	29	---	241	80	223	1162	37	319	---	322	---	417	---	---	67	1982
4	0.1	Y	43	---	292	111	352	1265	66	585	---	1006	---	644	---	---	151	1625
5	0.5	Y	27	---	179	78	294	395	53	244	---	303	---	307	---	---	44	606
6	1	Y	43	---	120	21	188	708	40	234	---	220	92	290	78	---	ND*	399
7	5	Y	45	---	203	2767	235	34682	65	464818	---	225	---	217	---	---	221	862
8	10	Y	54	---	321	5695	373	30302	88	590297	---	492	---	265	---	---	604	1426

*ND detection limit 200 ppb

NA - not available
C - column
F - filter

Spike - 400 ng of each compound was used in each run

TCB - 1,2,4-trichlorobenzene
TCT - 2,4,5-trichlorotoluene
LIN - lindane
ANT - anthracene
OCT - octachlorosytrene
MIR - Mirex
BEN - benzoperylene
PCB - Arochlor 1254 (PBCs)

CONCLUSIONS

Of the eight compounds evaluated in this study, four showed definite distribution behaviour between the columns and the filters. Highly chlorinated, high molecular weight hydrophobic compounds such as Mirex and octachlorostyrene were found exclusively on the filters. Low molecular weight, less chlorinated compounds such as 1,2,4 - trichlorobenzene and 2,4,5 - trichlorotoluene were found almost exclusively on the columns.

The methods used to recover the analytes require improvement. Measures must be taken to more effectively recover volatile compounds such as 1,2,4 - trichlorobenzene and unchlorinated high molecular weight compounds such as benzoperylene. It is also necessary to reduce interferences from the Balston filters. Each filter would require extensive solvent cleaning in a soxhlet extractor prior to use.

One solution to improve recovery efficiency is to use supercritical fluid extraction (SFE). This method allows selective extraction of a wide variety of compounds from complex matrices. It has the added benefit of reduction in time, labour and the use of toxic solvents. The use of SFE for this application requires additional research.

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DP6

COMPLETE AMBIENT AIR VOCs AND VOST POHCs ANALYSES USING ONE SINGLE TD/GC/MS SYSTEM

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INTRODUCTION

The determination of ambient air volatile organic compounds (VOCs) and industrial stack principal organic hazardous constituents (POHCs) is a complex task. This is due primarily to: 1. the wide variety of compounds of interest and 2. an ineffective means of analysis. At present, the US EPA suggested a core set of three methods for sampling and analysis of ambient air VOCs (1) and a thermal desorption / purge and trap gas chromatograph / mass spectrometeric (TD/PT-GC/MS) identification based procedure for the smoke stack POHC analysis (2). It is worth noting that compounds to be analyzed using these two methods are with similar boiling point ranges. Two sets of equipment are required in order to perform a complete VOC and VOST sample analysis.

In order to maximize the use of existing equipment, we have attempted to evaluate the possibility of using a VOST POHC analytical system to the analysis of ambient air VOCs with boiling point ranges from -30 to 200°C. The same system was used to do analysis on VOST POHCs with boiling point ranges from -30 to 200°C. Presented in this paper are the description of objectives and results obtained from this work. Preliminary results indicate that complete VOC and POHC analysis was possible on one single system. QA/QC data obtained from the VOST system give good recoveries and standard deviations for VOC compounds with boiling points from 10°C to 150°C.

EXPERIMENT

The VOST TD/PT-GC/MS analytical system consists of a Tekmar LSC2000 thermodesorber (Cincinnati, OH), a Tekmar 4210 autosampler, a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and a Hewlett-Packard 300 series data station. When operated in the VOST POHC analysis mode, a sparger was used to remove excessive water vapor in the VOST sampling cartridge (illustrated in Figure 1). For the ambient air VOC analysis, because relatively low moisture in the VOC sampling cartridge, the sparger was removed to form a thermal desorption / gas chromatograph / mass spectrometer system (TD/GC/MS).

An adsorbent analytical trap was used to concentrate both VOCs and POHCs for the subsequent GC/MS analysis. In the POHC analysis, the TD/PT-GC/MS used a standard Supelco adsorbent trap (Supelco Cata. # 2-0321, Oakville, Ontario). In the VOC analysis, a proprietary trap (3) was used in the TD/GC/MS system. Spiking mixtures were prepared using a modified gas mixing chamber (Lasale Glass, Barrie, Ontario). All data presented was obtained from both within run and between run experiments.

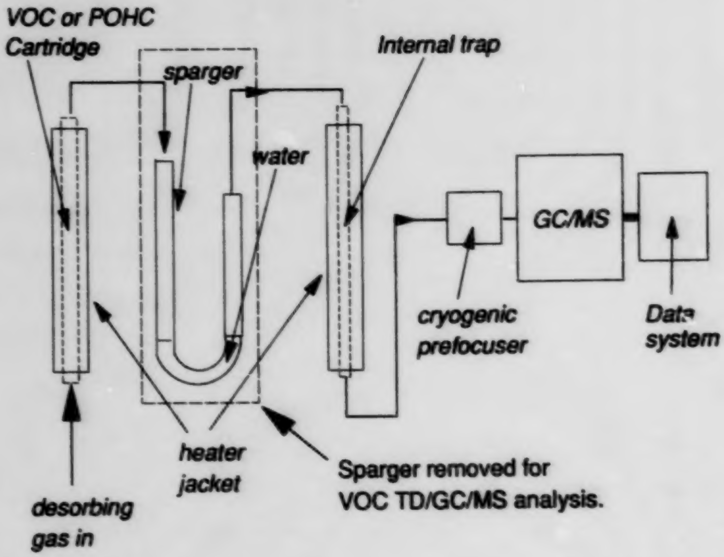
VOC or POHC
Cartridge
sparger
Internal trap
water
GC/MS
cryogenic
prefocuser
Data
system
heater
jacket
Sparger removed for
VOC TD/GC/MS analysis.
desorbing
gas in

Figure 1. Block diagram of TD/PT-GC/MS and TD/GC/MS for VOST POHC and ambient air VOC analysis, respectively.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the total ion chromatogram (TIC) obtained from the VOST TD/PT-GC/MS system. Figure 3 illustrates the TIC when operating this same system in the TD/GC/MS mode for the VOC analysis. Table 1 illustrates the evaluating results of the 26 VOST POHCs of the Ontario Ministry of the Environment (MOE). It is worth noting that both the low and the high boilers have much worse standard deviations than the compounds with boiling points from 10°C to 150°C. Each set of standard deviation data represents nine consecutive within run analysis of the 26 VOST POHCs. The analysis time, starting from the thermal desorption to the complete data analysis, was about 3 hours/sample. There was a time gap of 8 days between the collection of these two set of data.

Table 2 lists the evaluating results of 12 of the 36 VOCs in the MOE method (4). These 11 compounds were selected to represent a boiling point range from -32°C to 225°C. Again, one could obtain similar results to that from the 26 VOST POHCs.

CONCLUSION

We have demonstrated the ability of applying one single system to the analysis of both VOST POHCs and ambient air VOCs. Possibility of eliminate a cryogenic trap for the TD/GC/MS analysis offers a cost effective approach for the VOC analysis. Time required to convert a TD/PT-GC/MS to a TD/GC/MS, or vice versa, is about 30 minutes. One could dynamically allocate existing systems to smooth unexpected workload. Problems related to instrument downtime would have been alleviated, achieving a constant, maximized sample throughput.

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TABLE 1. QA/QC DATA OBTAINED FROM TD/PT-GC/MS SYSTEM FOR THE VOST POHC ANALYSIS.

	AMOUNT	STANDARD DEV.*	
COMPOUNDS (B.P., °C)	SPIKED (ng)	FIRST	SECOND
DICHLORODIFLUOROMETHANE (-29.8)	617.8	47.12	132.76
VINYLCHLORIDE (-13.9)	319.5	29.71	41.97
BROMOMETHANE (4.0)	485.4	N/A	N/A
TRICHLOROFLUOROMETHANE (24.0)	277.6	12.92	10.50
ACETONE (56.5)	118.7	163.27	67.06
1,1-DICHLOROETHENE (31.9)	182.7	2.33	6.74
TRICHLOROTRIFLUOROETHANE (46.0)	236.8	N/A	5.65
METHYLENE CHLORIDE (39.8)	198.8	22.12	23.16
TRANS-1,2-DICHLOROETHANE (48.0)	189.0	5.15	8.07
CHLOROFORM (61.0)	222.6	6.41	6.94
1,1,1-TRICHLOROETHANE (74.0)	200.6	9.94	10.88
1,2-DICHLOROETHANE (84.0)	188.4	4.10	5.16
BENZENE (80.1)	131.8	4.30	7.67
1,2-DICHLOROPROPANE (96.8)	174.0	4.38	7.98
TRICHLOROETHENE (86.8)	219.0	3.48	3.94
BROMODICHLOROMETHANE (90)	295.7	5.33	6.49
TOLUENE (110)	129.9	5.87	7.29
DIBROMOCHLOROMETHANE (119)	357.0	4.56	5.49
ETHYLENE DIBROMIDE (131	405.2	5.64	6.69
TETRACHLOROETHENE (121)	243.5	3.54	5.14
ETHYLBENZENE (136)	129.9	5.79	8.00
M/P-XYLENE (138)	129.5	6.30	10.90
BROMOFORM (149.5)	433.5	4.05	41.61
O-XYLENE (144)	132.0	6.29	10.51
CUMENE (169)	129.3	5.45	7.82
MESITYLENE (164)	129.6	41.54	14.32

* Presented in ±% to the spiked amount. There was an 8-day time gap between the first and the second set of data. Both sets of data were obtained from 9 within-run experiments.

TABLE 2. QA/QC DATA OBTAINED FROM TD/GC/MS SYSTEM FOR THE ANBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., oC)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*
METHYL CHLORIDE (-23)	103.3	21.4
VINYL CHLORIDE (-13.9)	136.8	16.22
1,3-BUTADIENE (-4.5)	97.5	17.41
1,1-DICHLOROETHANE (31.9)	182.7	19.02
TRICHLOROMETHANE (61)	222.6	29.3
BENZENE (80)	131.8	33.03
BROMODICHLOROMETHANE (90)	295.65	31.07
TOLUENE (110)	129.9	23.62
1,2-DIBROMOMETHANE (131)	405.11	30.48
CHLOROBENZENE (131)	166.11	21.05
1,2-DICHLOROBENZENE (180)	195.0	9.48
NAPTHALENE (217)	174.3	16.61

* Presented in ±% to the spiked amount. The data was obtained from 11 within- run experiments.

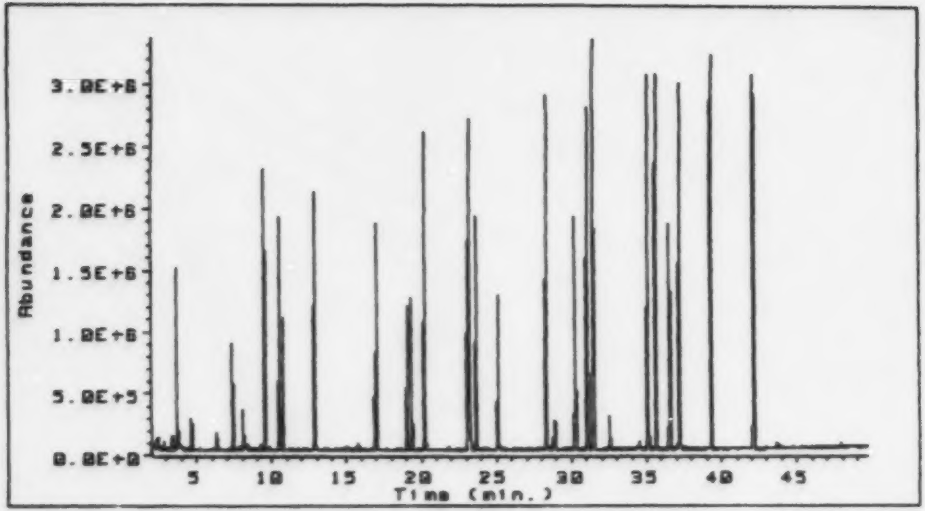

Figure 2: Total Ion Chromatogram obtained from the VOST TD/PT-GC/MS system.

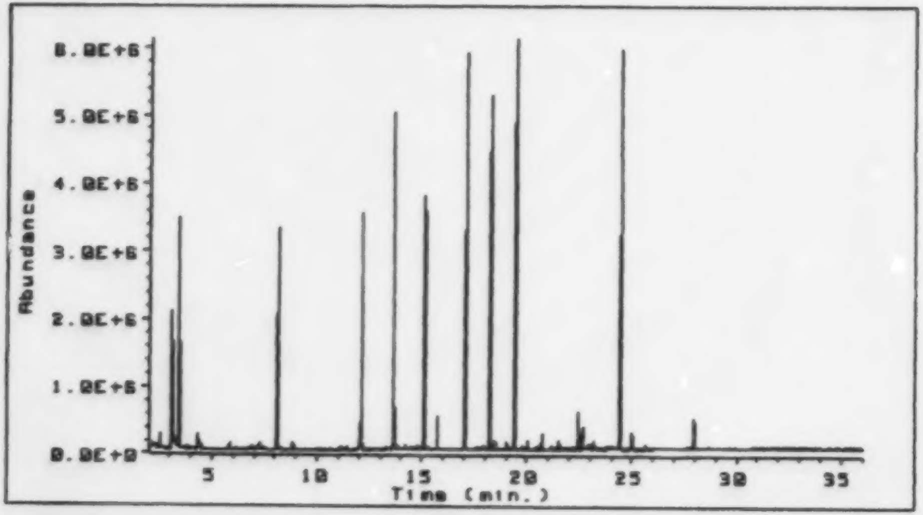

Figure 3: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system.

DP7

AN AUTOMATED GEL PERMEATION CHROMATOGRAPHIC METHOD FOR CLEANUP OF SEWAGE SLUDGE EXTRACTS FOR GC/MS ANALYSIS OF PRIORITY ORGANIC POLLUTANTS

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The increasing emphasis placed on water pollution and hazardous waste control, backed by stringent regulations such as Ontario's Municipal and Industrial Strategy for Abatement (MISA) program has increased the interest in the behaviour and fate of a wide range of organic contaminants during the wastewater treatment process. One result of this process is the annual production of approximately 7 million cubic meters of sludge. Treated sludges find many uses (1) including:

- co-disposal in landfill sites;
- agricultural land or land stabilization application;
- used as a fuel for low temperature incineration/power production;
- anaerobic digestion/evolution of methane gas;
- added to animal feeds (after suitable prescreening for contaminant levels).

Given these potential uses and the fact that many organic chemicals which enter wastewater treatment systems are ultimately retained in the sludge it is important to establish the nature and concentrations of these pollutants.

To satisfy the needs of investigative and regulatory environmental monitoring, the TO section of the LSB has been developing a rapid GC/MS method for the analysis of sewage sludges. Organic compounds investigated include:

- 40 base neutrals;
- 20 phenolics;
- 7 phenoxy acid herbicides;
- polychlorinated Biphenyls;
- 30 chlorinated hydrocarbons (pesticides and industrials).

These target organic compounds may be present in sludges (2) either in: solution, colloidal suspension, or absorbed on particulate matter.

This coupled with the chemical complexity of sludge, including high and variable organics and solids content, present major problems in the determination of trace levels of organic priority pollutants.

The objective of this research project was to develop an effective, and rapid analysis procedure which would quantitatively extract the target components, and consistently separate them from the co-extracted interferences including lipids, fatty acids, hydrocarbons and other high molecular weight compounds (3). Gel Permeation Chromatography (GPC) is a widely used technique in biochemical analysis and a large number of papers had been published [4-11] describing the cleanup of environmental sample extracts such as fish, sludge, solid waste, soil and sediments. In this regard the application of Gel Permeation Chromatography (GPC) was evaluated and an automated rapid cleanup procedure was devised.

Experimental

Apparatus - Schimadzu High Performance Liquid Chromatograph equipped with a SIL-6B Autoinjection (modified with a 2 ml injection loop) and Advantec SF-2120 Superfraction collector.
Column - 600mm x 30mm packed with 60g of Bio-Beads SX3 (Bio-Rad Laboratories).
Elution Solvent - Methylene chloride-cyclohexane (1:1,V/V) flow rate 2 ml/min.
Calibration mixture - A standard mixture was prepared by dissolving Di-n-octylphthalate, Benzyl butyl phthalate, Methoxychlor and 4-nitrophenol in Methylene chloride ($5 \mu g/mL$) of each compound).

Sample Preparation

Sewage sludge(s) varying in consistency from 0-20% solids was homogenized and a 25g portion was extracted with a mixture of solvents (Diethylether/methylene chloride 2:1, V/V). The extract was concentrated to 2 ml. A 0.5 ml extract was injected in the GPC system for cleanup.

Results and Discussion

- In our preliminary studies, two conventional open column chromatography cleanup approaches were evaluated using a Gel Permeation Chromatography (Bio-Beads SX) and polarity separation (Florisil).

- Qualitative GC/FID screening of the extracts cleaned on Bio Beads SX (collecting one fraction) do not appear much different from those of extracts cleaned up by Florisil Column Chromatography. Both of these extracts proved to be too complex (i.e. too much interfering material) to analyse by GC/MS.

- The cleanup on Bio-Beads SX was repeated employing an HPLC system.

- The packings and solvent system evaluated were:

  Bio-Beads SX2 - Methylene Chloride
  Bio-Beads SX3 - Methylene chloride/cyclohexane (1:1,V/V)
  Bio-Beads SX8 - Methylene chloride/cyclohexane (1:1,V/V)
- Bio-Beads SX3 - gave the best results and was selected for further work.

Collecting all our target compounds in one fraction gave unsatisfactory results, so a fractionation procedure was developed. In order to calibrate the system and determine the optimum fractionation window size, the standard mixture was separated on the Gel Permeation Chromatography system.

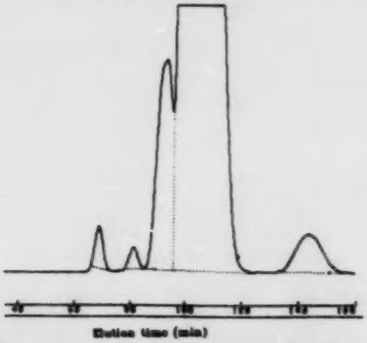

Fig. 1 - GPC elution profile of a standard mixture eluted with CH2CL2/CYCLOHEXANE (1:1) on Bio-Beads SX-3(60g)

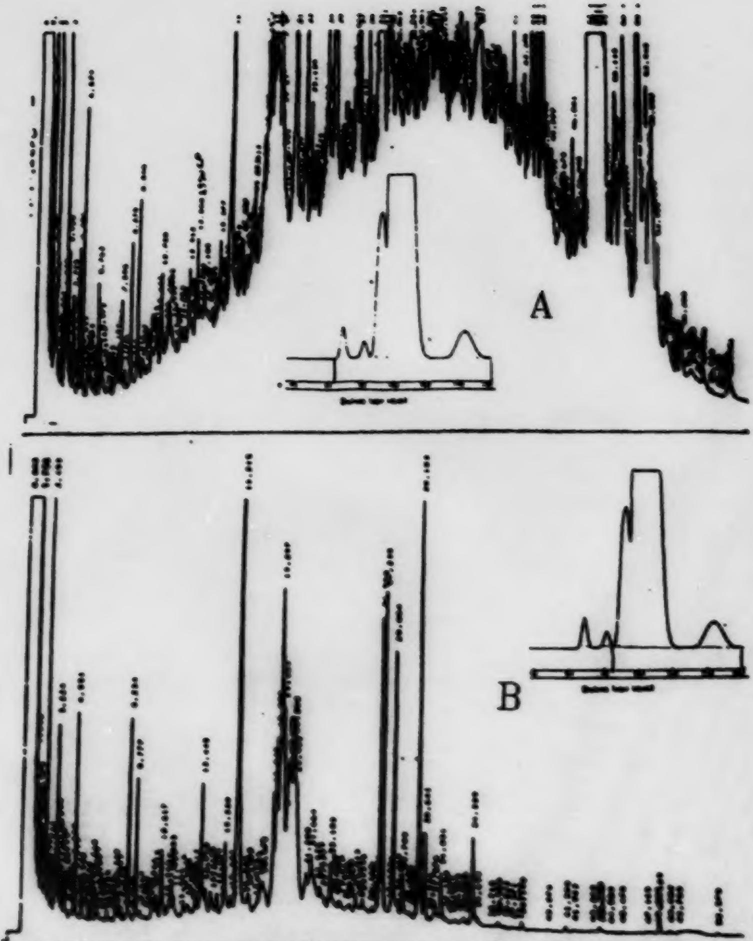

Fig. 2 - Flame ionization Gas Chromatograms of a sludge extract cleaned up by GPC: A - total collected, B - Fraction II

Two fractions were collected.

Fraction I from 62 min (when the first compound Di-n-octylphthalate elutes) to 82 min (at the valley between benzyl butyl phthalate and the Methoxychlor).

Fraction II collected from 82 min (when Methoxychlor elutes) to 157 min (after our last eluting compound 4-nitrophenol).

Fraction I contains all phthalates as well as the majority of interferences.
Fraction II contains all of the target compounds.

To illustrate the advantage of GPC fractionation procedure, see Fig. 2.

Summary and Conclusions

- This work is part of the effort to develop an analytical method for the determination of a wide range of organic contaminants in STP sludges.

- A number of GPC packing (Bio-Beads) for the cleanup of sludge extracts were investigated, ranging from SX3 to SX8.

- Bio-Beads SX3 were confirmed as the resin of choice for this type of work, in agreement with other researchers.

Sacrificial separation of a first fraction containing mainly phthalates virtually eliminated interferences from second fraction containing all other target priority pollutants.

- Separation conditions were optimized and then automated to provide an extract suitable for direct GC/MS analysis.

- The sacrificed fraction can be utilised for the analysis of phthalates after further cleanup on Florisil.

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DP6

SIMULTANEOUS DERIVATIZATION - EXTRACTION TECHNIQUE FOR THE ANALYSIS OF ACIDIC ORGANIC CONTAMINANTS FROM WATER - FEASIBILITY STUDY WITH DIAZOMETHANE FOR THE ANALYSIS OF 4-AMINO - 3,5,6-TRICHLOROPICOLINIC ACID (PICLORAM)

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Picloram (4 amino-3,5,6-trichloropicolinic acid, is a herbicide widely used, for the control of woody and broad leaf plants in pastures, small grains, timberland and various rights of way.

Even though Picloram is highly active at low application rates, is relatively non-toxic to animal species; its wide-spread usage and resistance to degradation raises concerns regarding environmental levels and fate. Various procedures have been developed to determine residues of Picloram in soil, plants, sediments and water. Techniques such as High Performance Liquid Chromatography (HPLC) suitable for the analysis of commercial formulation without derivatization as well as Gas Chromatographic methods which typically determine Picloram as the methyl ester, 2-chloroethyl ester or pentafluorobenzyl derivative. For multicomponent environmental analysis, solvent extraction followed by derivatization and gas chromatographic analysis is the most common technique. However, the performance of these methods, especially in the area of multicomponent environmental applications can be highly erratic and biased low. Recoveries reported by various authors vary from 97(1) to 59(2) percent and it is not uncommon to find values lower than these.

This paper describes the development of a rapid, simultaneous extraction - derivatization procedure (3) for the analysis of picloram in water which provides consistent (>86%) recoveries. The research finding also provides an insight into the possible source of analytical variability related to the chemical properties and equilibrium of Picloram in aqueous solution.

Experimental

Apparatus - Gas Chromatograph Hewlett Packard 5730 with dual Ni63 electron capture detectors. The instrument is fitted with one split/splitless capillary injector system, HP7672A autosampler, HP33804 dual pen strip chart recorder, all interfaced with the HP1000 computer system.

Columns - capillary columns 30m x 0.25mm D1701 and DB1.
Temperature program: initial 90 C, hold 2 minutes programming rate 4 C/min, hold at 270 C for 8 minutes. Injector temperature 250 C, Detector temperatures 300 C.

Procedure - unless otherwise stated all experiments were carried out under the following conditions:

- The water spiked or containing the target analytes sample (800 ml) was acidified (HCl) to pH1.

- Dichloromethane (30 ml) was added and mixed well.

- Diethylether (60 ml) was added and mixed well.

- The two layers were allowed to separate and diazomethane (DAM) solution 1 ml (prepared from 21,5g of N,N-Dimethyl N,N-Dinitrosoterephthalamide made up to 37 ml with diethyl ether) was added with a pipette to the top solvent layer in a circular motion.

- The reaction mixture was allowed to stand for 10 minutes.

- The mixture was shaken well and diazomethane addition was repeated twice.

- The mixture was allowed to stand for 2 hours.

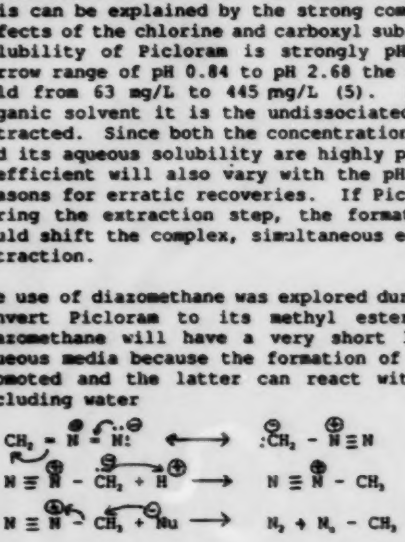
After this, the organic layer was separated and concentrated on a rotary evaporator (addition of more methylene chloride will sink the solvent to form a bottom layer if this is more convenient to separate).

Results and Discussion

Chemical Consideration

Superficial examination of the chemical structure of Picloram, a carboxylic acid with two different amino functions, would make one conclude that it has amphoteric properties. In practice, Picloram behaves as a fairly strong organic carboxylic acid and significant protonation of the amino functions does not occur above pH 0.8. This can be explained by the strong combined electron withdrawing effects of the chlorine and carboxyl substituents (4). The aqueous solubility of Picloram is strongly pH dependent. Even in the narrow range of pH 0.84 to pH 2.68 the solubility increases seven fold from 63 mg/L to 445 mg/L (5). During extraction with an organic solvent it is the undissociated form of Picloram that is extracted. Since both the concentration of undissociated picloram and its aqueous solubility are highly pH dependent, the partition coefficient will also vary with the pH. This may be one of the reasons for erratic recoveries. If Picloram could be derivatized during the extraction step, the formation of a neutral species would shift the complex, simultaneous equilibria in favour of the extraction.

The use of diazomethane was explored during the extraction step to convert Picloram to its methyl ester. It is expected that diazomethane will have a very short lifetime in strong acidic aqueous media because the formation of the protonated reagent is promoted and the latter can react with most nucleophile ($Nu^{\ominus}$) including water



$$CH_2 = \overset{\oplus}{N} = \overset{..\ominus}{N}: \longleftrightarrow :\overset{\ominus}{C}H_2 - \overset{\oplus}{N} \equiv N$$

$$N \equiv \overset{\oplus}{N} - \overset{\ominus}{C}H_2 + H^{\oplus} \longrightarrow N \equiv \overset{\oplus}{N} - CH_3$$

$$N \equiv \overset{\oplus}{N} - CH_3 + \overset{\ominus}{N}u \longrightarrow N_2 + Nu - CH_3$$

The presence of extraction solvent in the aqueous reaction mixture will protect diazomethane from rapid decomposition and permit the target reaction to proceed with less competition from non target nucleophiles.

Even if little methyl ester formation takes place in the aqueous phase, portion wise addition of diazomethane to the solvent layer will esterify the already extracted Picloram and extraction of a further quantity of Picloram can begin once again without removing the solvent.

Thus while minimizing the effects of pH on the process, addition of 2-3 portions of diazomethane solution (followed by thorough mixing) becomes practically equivalent with extraction by 2-3 aliquots or organic solvent see Table 1 and 2.

Table 1

RECOVERY OF PICLORAM (SPIKING LEVEL 1ppb) USING DIFFERENT ACIDS AND SIMULTANEOUS DERIVATIZATION/EXTRACTION PROCEDURE.

Acid used at pH (1-2)	% Recovery
H_3PO4	102
HCL04	110
HC004	40
H_2S04	98,89
HCl	97,106,83*
	*Diazomethane added in 1 portion

Recoveries of seven acid herbicides from fortified 800 ml water samples are presented in Table 2.
The recoveries of all seven herbicides were good and ranged from 77 to 111%.
Recovery reproducibility proved excellent.

Table 2

RECOVERIES (%) OF ACID HERBICIDES FROM FORTIFIED (APPROX. 1μg/L LEVEL) 800 mL WATER SAMPLES BY SIMULTANEOUS EXTRACTION DERIVATIZATION PROCEDURE

	DAM three portions									DAM one portion	
HERBICIDE	#1	#2	#3	#4	#5	#6	#7	AVG	SD	#1	#2
DICAMBA	95	88	90	99		93	97	94	4	87	97
24DP	99	95	98	102	77	97	98	95	8	101	99
24D	111	104	110	113	95	112	111	108	6	116	111
SILVEX	105	100	101	104	86	95	100	99	6	108	95
245T	107	104	105	107	100	101	102	104	3	112	106
24DB	108	104	105	107	104	103	103	105	2	114	107
PICLORAM	101	105	106	100	100	97	97	101	3	86	77

The results in Table 2 show the application of the simultaneous extraction-derivatization procedure to acidic compounds in the full scan including Picloram. The generally excellent recoveries indicated a wide applicability for this technique. Further study is underway for the use of this simple and effective method for other groups of acidic compounds, such as resin and fatty acids. Preliminary results are most encouraging.

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Brominated and Mixed Bromo/Chloro Dibenzo-p-dioxins and Dibenzofurans: Toxicological Properties, Analytical Methods and Occurence

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INTRODUCTION

Considerable information has accumulated over the past two decades regarding the synthesis, analytical methodology, environmental distribution and biological activity of polychlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs). CDDs and CDFs are known to exist as trace contaminants within certain commercial products prepared from chlorinated phenols (and their phenoxy acid derivatives), polychlorinated biphenyls (PCBs), and other chlorinated aromatic compounds. In addition to these chemical sources, CDDs and CDFs are also derived from burning and other high temperature processes and are considered to be associated with combustion whenever organic materials and a suitable source of chlorine are present.

In contrast, very little has been reported concerning the potential environmental importance of polybrominated dibenzo-p-dioxins (BDDs), dibenzofurans (BDFs) and mixed bromo/chloro dibenzo-p-dioxins and dibenzofurans (CBDDs and CBDFs). These classes of compounds are of interest owing to their structural similarities to the CDDs and CDFs. Furthermore, BDDs and BDFs are also found as impurities in commercial products (eg. brominated flame retardants) and both BDDs/BDFs and CBDDs/CBDFs have been observed as thermal reaction products from the appropriate precursors. Lastly, these classes of compounds are expected to exhibit biological activity similar to their chlorinated analogues and hence their presence in the environment is a cause for concern.

TOXICOLOGICAL/BIOLOGICAL EFFECTS

There is very little information in regards to the toxicity of these compounds, however the data that is available indicates that some of the congeners do pose a potentially significant health hazard. For example, in guinea pigs 2,3,7,8-tetrabromodibenzofuran has been found to be as potent as its chloro analogue (2378-TCDF) and their toxic symptoms are similar. In the rat 2,3-dibromo-7,8-dichlorodibenzo-p-dioxin is more toxic than 2,3,7,8-TCDD and 2,3,7,8-TBDD is equipotent with 2,3,7,8-TCDD.

SOURCES/OCCURENCE

BDDs and BDFs have been detected in many of the brominated flame retardants and also in their pyrolysates. Moreover, when brominated flame retardants are mixed with chlorine containing plastics (eg. PVC) and pyrolysed CBDDs and CBDFs are formed.

Recently, as expected, these compounds (BDDs, BDFs, CBDDs, CBDFs) have also been found in ash samples from an MSW incinerator although the levels are much lower than the CDD and CDF levels.

ANALYTICAL PROCEDURES

From the available literature, it would appear that the methods commonly used for CDD/CDF analysis can be used for the analysis of the bromo and mixed bromo/chloro analogues. GC/MS would appear to be the instrument of choice for final detection and quantitation.

Capillary GC would be preferred due to the number of theoretically possible congeners involved; there are 1550 CBDDs and 3050 CBDFs possible. Also, due to the molecular weights of some of the congeners high resolution MS would be more suitable than quadrupole MS.

Currently, there are standards, including C13-labelled surrogates, available from two sources. These compounds are very difficult to prepare in good quantities and are also somewhat unstable.

DP10

DETERMINATION OF ORGANOLEAD COMPOUNDS IN INDUSTRIAL EFFLUENTS

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SUMMARY

Organolead compounds are used as "anti-knocking" agents in gasoline to increase the efficiency and longevity of high compression engines. The toxic affect of these compounds on humans is well known. Governments in North America have now restricted the use of these compounds in gasoline, however many other parts of the world such as Europe and Asia have not. In Ontario, these compounds are produced for export overseas.

The Ontario Ministry of The Environment has set guidelines for the amounts of organolead compounds in industrial effluents. The Ministry has developed a method for analyzing these compounds for regulation monitoring. This paper describes the development of this method, instrumental optimization, in-situ derivitization/extraction and quality control data.

INTRODUCTION

Despite the benefits of organolead as an octane enhancer and a valve seat lubricant, scientific research has demonstrated conclusively that negative health and detrimental environmental effects of lead far outweigh it's advantages as a gasoline additive. Acute lead poisoning has been reduced in North America because of the use of "unleaded gasolines". However, chronic exposure to low levels of lead in the environment still remains a serious concern. In the mid 1980's, governments in North America restricted the use of lead in gasoline. Farm and aviation fuel are the only known exceptions. Although organolead compounds are not being used locally in gasoline, they are still being produced for export overseas in Ontario. The municipal and industrial strategy for abatement (MISA) program incorporated by the Ontario Ministry of the Environment dictates that it is the responsibility of the industry or municipality to monitor and control, to provincial guidelines, the concentration of pollutants in their effluent. Regulation monitoring is conducted by the Ministry on a random basis to assure the company is conforming to the provincial guidelines. For this purpose, the Laboratory Services Branch has developed a method for analyzing organolead compounds in industrial effluent.

Methods available for the determination of alkyl lead compounds include spectrophotometric measurements of their dithizonates in chloroform at different wavelengths[1], and of their dialkyllead complexes with 4-(2-pyridylazo)resorcinol after conversion of the trialkyl lead to dialkylead with iodine monochloride[2].These methods are lengthy and lack speciation.

Other methods include gas chromatography (GC) with an electron capture detector[3], gas chromatography - microwave induced plasma - atomic emission detection (GC-MIP-AED)[4], and gas chromatography - atomic absorption spectrophotometery (GC-AAS)[5]. All of these methods use an extraction of lead compounds from an aqueous solution after chelation with appropriate reagents.
The combination of gas chromatography and atomic absorbtion spectrophotometry has proved to be an excellent technique for the determination of the above compounds because of its sensitivity and the ability to speciate and will be used for this method. The compounds to be analyzed are tetramethyl (Me_4Pb), tetraethyl (Et_4Pb), trimethyl (Me_3Pb), triethyl (Et_3Pb), dimethyl (Me_2Pb) and diethyl (Et_2Pb) lead.

EXPERIMENTAL

A Hewlett Packard 5890 Gas Chromatograph (GC) equipped with a Supelco megabore fused silca DB1 capillary column (30 m in length X 0.530 mm I.D. - 1.4 um film thickness) was used for separation. The transfer line was constructed of 1/16" I.D. stainless steel tubing about 3 ft in length. The quantitation was performed by using a Perkin-Elmer 2380 atomic absorption spectrophotometer (A.A.) with a quartz furnace for atomization. The data was recorded on a Varian 7240 integrator.

The operating conditions for the GC were set at 150 degrees celsius for the injection port temperature and 0 - 200 degrees celsius for the oven temperature at programmed stages. The transfer line was heated to 70 degrees celsius with nitrogen carrier gas flowing through at 10 ml/min. The A.A. wavelength was set at 217.4 nm with a slit width of 0.7 nm. The quartz furnace was heated to 900 degrees celsius.

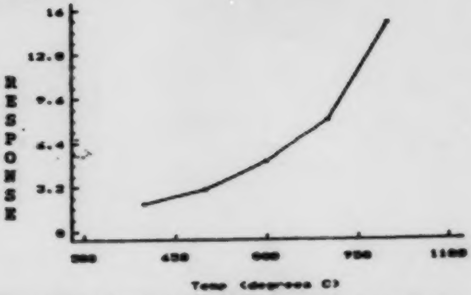
Sample Storage and Preparation

The samples were received in 1 litre amber glass bottles lined with teflon caps. They were stored at 4 degrees celsius and the analysis was performed within 2 weeks. The sample preparation involved removing a 10 - 11 ml sample and displacing it with 10.0 ml of hexane. The bottle was capped and rotary tumbled for 30 min. The organic phase was separated, dried with anhydrous sodium sulphate and analyzed. The volume of the remaining sample was adjusted to 800 ml. Sodium chloride (50 g) and aqueous 0.5M sodium diethyldithiocarbamate (50 ml) were added to the sample. The solution was extracted with 2 X 50 ml hexane. It was rotary tumbled for 30 min with each extraction. The organic phase was separated and dried with sodium sulphate. Toluene (4 ml) was added to the extract and then it was concentrated to 3 - 4 mls. Butyl Grignard reagent (Aldrich, 1.9M in THF) at a volume of 0.5 ml was added, mixed and kept at room temperature for 10 min. The volume was adjusted to 5.0 ml with toluene. It was then cooled in an ice bath and washed with 4-5 ml of 0.5M sulphuric acid to destroy the excess Grignard reagent. A portion of the extract was dried with sodium sulphate and analyzed for trialkyl and dialkyl lead compounds.

RESULTS AND DISCUSSION

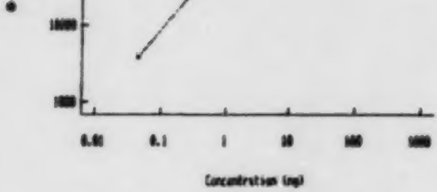
1. **Instrument Optimization.** The optimization of the instrumentation included injection port temperature, carrier gas flowrate, oven temperature, A.A. slit width, A.A. wavelength, furnace temperature, furnace alignment, hydrogen flowrate and transfer line temperature. The most critical parameter was furnace temperature. An optimum was not reached due to the thermal breakdown of the furnace winding. Consequently, optimum sensitivity is not achieved. More experimentation with a heavier gauge furnace wire will be conducted in the future. A compromise temperature of 900 degrees celsius was used. A response profile for several furnace temperatures is shown in FIG 1.

FIG 1. Profile - Response VS Furnace Temperature
50 ppb Tetraethyl Lead



2. **Linear Dynamic Range.** The linear dynamic range was determined to be approximately 3 orders of magnitude from the instrument detection limit. FIG 2. shows a response while varying concentrations of tetraethyl lead.

FIG 2. Concentration VS Response - 50 ppb Tetraethyl Lead



3. Quality Control Data.

Recovery studies were performed by spiking double distilled water samples at 20 and 50 ug/l. Eight replicates were spiked and analysed and the data is given in Table 1 and Table 2. The method detection limits (MDL'S) were determined to be 0.5 to 2.0 ug/l and were calculated according to method development protocol[4]. The quality control data on dialkyl lead compounds was not available because of the lack of pure standards. Future attempts to synthesize purer standards will be conducted.

Table 1. Recovery Data @ 20 ug/l. n = 8 replicates

Parameter	Recovery(%)	%RSD	MDL(ug/l)
Me_4Pb	87 - 96	11	0.8
Et_4Pb	80 - 112	21	2.0
Me_3Pb	90 - 104	2	0.5
Et_3Pb	85 - 110	9	1.0

Table 2. Recovery Data @ 50 ug/l. n = 8 replicates

Parameter	Recovery(%)	%RSD	MDL(ug/l)
Me_4Pb	93 - 96	5	0.5
Et_4Pb	90 - 106	10	2.0
Me_3Pb	90 - 114	10	1.5
Et_3Pb	85 - 110	8	1.0

The method was successfully tested on an actual industrial effluent. The data obtained by standard addition in six industrial effluents was found to be within the limits reported in Table 1 and Table 2.

CONCLUSIONS

1. The instrumental optimization was performed. The furnace temperature of the A.A. was found to be the most critical parameter on sensitivity.

2. A method has been established for the analysis of tetra alkyl and tri alkyl lead compounds. Detection limits, linear dynamic range, precision and extraction efficiency data were within the MISA methods development protocol.

3. Work for the determination of di alkyl lead compounds is in progress.

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DP11

TECHNIQUES FOR THE IDENTIFICATION OF SPECIFIC SOURCES OF AIRBORNE PARTICULATES

J. Hipfner, R.R. Martin, R. Moody, T. Lee, M. Guiliacci

Introduction

Source identification for airborne particulates is important both to insure effective remedial action and to assess potential health risks associated with specific air masses. Three methods for source identification are especially promising: elemental isotope distribution, trace element distribution and surface reactivity of the particles. A wide variety of experimental techniques are available at The University of Western Ontario including Secondary Ion Mass Spectrometry (SIMS), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) and Ion Chromatography (IC). Other techniques are available such as Neutron Activation Analysis (NAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). We have confined our initial studies to the instruments readily available at The University of Western Ontario or at the Ontario Ministry of the Environment Laboratories. In addition we have sought to focus attention, where possible, on instrumentation which can be used in simple tests with a relatively unskilled operator. The main thrust of the report will be to examine the results obtained by IC and SIMS, the former is by far the easier technique. Some ICP-MS will also be reported

We have established that XPS and SEM were of limited utility without detailed study. XPS results are limited because the technique is surface sensitive (i.e. to two or three monolayers), the samples are prone to charging and are widely distributed on the filter surface. SEM has high detection limits (~ 1%) and with current instrumentation is not capable of detecting carbon, an element of special interest because it is abundant in atmospheric particles originating from combustion. FTIR showed the principle species in assemblies of particulate matter to be NH_4NO_3 and $(NH_4)_2SO_4$, though organic functional groups such as carboxylates could be identified. The area will be pursued more vigorously in the future. NAA studies are underway but the technique is expensive, time consuming and produces low-level nuclear waste.

Finally early SIMS measurements show that there is insufficient material in a normal air sample to carry out isotopic analysis of the surface material. Accordingly we have chosen to study elemental distributions using SIMS imaging techniques. In addition we have chosen to assess the surface reactivity of air particulate material by measuring catalytic activity on the reaction: $SO_3^= \longrightarrow SO_4^=$.

This reaction was chosen because it has interesting environmental consequences (acid rain), may be indicator of the potential health effects of atmospheric particles and is easily followed using IC.

Experimental

1. Sample Collection

Sample were collected on glass fibre filters using high volume samples, by the Ontario Ministry of the Environment.

2. Trace Metal Analysis

Trace metal concentrations were obtained using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. For each filter, two samples were made. The samples were prepared to determine the total metal concentration and the concentration at pH 5. The samples prepared for total metal determination was made by leaching a filter in 3% nitric acid for 30 minutes and filtration through a 0.8 µm Nucleopore filter. The samples prepared for metal determination at pH 5 were made by leaching the filter at pH 5 for 30 minutes and subsequent filtration through a 0.8 µm Nucleopore filter with stabilization in 0.5% nitric acid (100 µl of 35% nitric acid in 7 ml sample).

3. Ion Chromatography and the $SO_3^{2} \longrightarrow SO_4^{=}$ Reaction

The oxidation of S(IV) is pH dependent with the exact reactive species depending on the nature of the equilibrium system[1-6]. However, it is generally agreed that the oxidation of S(IV) to S(VI) decreases as the aqueous phase becomes acidic[7]. Since the reaction is highly pH dependent, a buffer was used to control the pH. The buffer chosen was a 10 mM $CH_3CO_2^-/CH_3CO_2H$ buffer at pH 4.7, standardizing all the S(IV) oxidation tests.

The S(IV) oxidation test consisted of analyzing two planchets from one filter. Assuming the distribution of material on the filter was homogeneous, one piece of filter was used as the blank to determine the initial concentrations (or loadings) of the anions present (Cl^-, NO_3^-, SO_3^{2-} and SO_4^{2-}) on the filter and the other was used to test the S(IV) oxidation reactivity in a buffered solution. The blank sample was prepared by immersing the filter in 10.00 ml of distilled-deionized water (DDW). The second piece was immersed in a 0.01 M acetic acid/acetate buffer with a pH of 4.7 and the addition of SO_3^{2-} stock to approximately 15 ppm. The pH was measured with a Hanna Piccolo portable pH meter. The samples were allowed to react for approximately 24 hours in the dark.

The samples were analyzed by ion exchange chromatography (IC) to determine the concentration of the anions present. The liquid samples obtained from the filters were passed through a 0.8 µm Nucleopore filter to remove any large particles before injection into the ion exchange column. The ion chromatograph used was a hybrid consisting of a Dionex AS4 analytical column and a Dionex membrane suppressor as the eluent suppressor. The eluent used was 1.6 mM HCO_3^-/CO_3^{2-} buffer at a flow rate of 2.2 ml/min. The eluting ions were detected with a Waters conductivity detector.

The S(IV) stock was prepared by dissolving Na_2SO_3 salt (BDH Chemicals). It was found there were significant amounts of Na_2SO_4 (7 to 15% by weight) already present, varying from stock to stock. In addition, it was found that the S(IV) stock solution was unstable decomposing at a rate of 10 to 15% per day. As a result, the S(IV) stock solution was made up fresh and calibrated by oxidizing the S(IV) and S(VI) with H_2O_2 and back calculated against sulfate standards.

4. SIMS Analysis

SIMS analysis was carried out using a CAMECA IMS 3f instrument with a O^- primary beam rastered over a 400 × 400 μ area while secondary ions for imaging were collected from a central circular spot 250 μ in diameter. The primary beam was at a current of 100 nA with 7.5 keV net energy. The filters selected for imaging were those which showed high catalytic activity in the $SO_3^=$ oxidation reaction.

Results and Discussion

The results indicate that specific groups of filters show rapid $SO_3^=$ oxidation to a degree which is significantly greater than that of other filter material. Generally, but not always, the reactive filters are shown by ICP-MS to be rich in metals, especially iron, manganese and nickel. In addition there are groups of filters that show significantly reduced levels of $SO_3^=$ conversion. This latter effect may be due to organics which are preferentially oxidized by dissolved oxygen or to either organic or inorganic chelating agents (i.e. carboxylic acids or phosphates) which chelate metal ions in solution.

Metal ion and metal catalyzed oxidation of S(IV) have been observed to increase oxidation rates, but the exact nature of the interaction is not well understood(1). Such catalysts include iron, manganese, titanium, vanadium, copper and nickel(1-4). In addition, it is known that graphitic carbon can also catalyze S(IV) oxidation(8). As well, S(IV) oxidation is believed to be light sensitive(9).

SIMS imaging(10) can be used to infer the chemical state of various elements on the filter surface. Thus Pb occurs in association with Br, probably the product of automobile exhaust containing Pb and Br from free radical scavengers added to the gasoline. Aluminosilicates can be readily recognized which are either crustal material (wind erosion) or the products of fossil fuel combustion. Interestingly P and F are often associated with the aluminosilicate material. This is suggestive of fertilizer (in the form of phosphate) while F may originate from $Ca_5(PO_4)_3F$ or as a byproduct of aluminium smelting.

Conclusions

The correlation between the metal concentrations and $SO_3^{=}$ conversion shows that filters with the highest metal concentrations also have the highest conversion. This suggests that the oxidation of S(IV) in the chemical reactivity test in some of these filters is metal catalyzed. More significantly the wide variability in the reactively of the filter material in contact with $SO_3^{=}$ solutions shows that the reaction, in concert with IC, can be used to identify air masses which pose significant health hazards either by their direct effects or by the atmospheric chemistry they induce. As well, unusual activity may well be characteristic of the source of the particulate material.

The SIMS results show that ion imaging can be used to elucidate the chemistry of particulate material, which in turn serves as an indication of the source of the material.

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VOLUME II

SESSION E

ENVIRONMENTAL SOCIO-ECONOMICS RESEARCH

VERBAL PRESENTATIONS

TRADABLE PERMITS
FOR THE CONTROL OF SULPHUR OXIDES IN CANADA

BY CHARLES D. MALLORY

OCTOBER 1990

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ABSTRACT

In the economic literature, tradable permit systems have been shown to resolve certain environmental problems "efficiently". These are seldom found in practice, however; could such a program be useful for the control of acid rain in Canada? In this paper, the problem of market structure is examined by way of a numerical example involving two large firms. What emerges is that the firms will have different preferences as to the distribution rule. As well, when the market is concentrated, as in Canada, the properties of economic efficiency cannot be guaranteed for régimes based on free distribution of permits to pollutant sources. It is also shown that a zoned emission permit system would appear to be the most useful in the Canadian situation.

RÉSUMÉ

Dans la littérature économique, il est établi que des programmes de droits d'émissions échangeables puissent résoudre certains problèmes environnementaux de façon "efficace". Cependant, on ne les retrouve pas souvent dans la pratique; est-ce qu'un tel programme pourrait être utile pour le contrôle des émissions acides au Canada? Dans ce papier, le problème de la structure du marché est examiné par le biais d'un exemple numerique impliquant deux grandes firmes. Ce qui sort, c'est que les firmes n'auront pas les mêmes préférences quant à la règle de distribution des permis. Quand il y a peu de firmes polluantes, comme au Canada, il est aussi démontré que la distribution gratuite a peu de chances de respecter les critères d'efficacité économique, si les droits sont distribu/s gratuitement. Les droits d'émissions par zone s'avèrent les plus utiles dans le contexte canadien.

1 THE BASIC MODEL

A reader familiar with the economics literature relating to environmental problems might find it puzzling that economically efficient tools for the control of pollutants, such as taxes and permits, are hardly used in the real world. The efficiency characteristics of these methods, which imply easier accomodation of growth and incentives to innovate as well as lower costs of control, seem so straightforward that this question deserves greater study.

The object of this paper is to bridge the gap between the theoretical and the practical, making special reference to the problem of sulphur oxides (perhaps the dominant cause of acid rain) in Canada. The aspects of the Canadian situation that are highlighted are the potential dominance of a small number of large emitters and the importance of provincial jurisdiction. Study of the latter question fits well also with the considerable regional disparity in deposition rates.

The theoretical foundations are set out in a simple mathematical model, establishing the standard marginal efficiency conditions on which the economists' case rests. Issues related to market structure are examined using a numerical example involving two firms. Several questions hinge on the initial allocation of permits and their cost. In the last section the regional aspects are discussed.

The economy can be represented by a simple model involving just two nearby firms. The firms have different production processes, for example electricity generation and metal smelting, thus their cost structures are different. The duopolistic nature of the market for pollution rights in this example is apparent and important, forming the basis of the arguments in the next section; however, the firms are competitive in other factor markets. In the first instance it will be supposed that there are no regulations for the control of atmospheric emissions; a permit market involving a 50% reduction in allowable emissions will then be considered.

E represents the production technology of one firm, which uses a vector of inputs $\mathbf{x} = x_1,\ldots,x_n,\ldots,x_N$, as well as producing sulphur oxides, denoted by s. This may be presented as

$$E\ (\mathbf{x}^E,\ s^E) = 0 \qquad \text{<1>}$$

Similarly, M represents the technology of the other firm, so that:

$$M\ (\mathbf{x}^M,\ s^M) = 0 \qquad \text{<2>}$$

Firms maximize profits (π) by using inputs in the most efficient combination. The problem of this small "economy" can be solved jointly, using the following Lagrangian expression:

$$\max \pounds = \mathbf{p}\ (\mathbf{x}^E + \mathbf{x}^M) - \mu\ [E\ (\mathbf{x}^E,\ s^E) + M\ (\mathbf{x}^M,\ s^M)] \qquad \text{<3>}$$

where prices are represented by the vector $\mathbf{p} = (p_1,\ldots,p_n,\ldots,p_N)$.[1]

For any given input x_n, profit maximization implies;

$$p_n = \frac{\delta E}{\delta x^E_n} = \frac{\delta M}{\delta x^M_n} \qquad \text{<4>}$$

This standard result means that the use of any input x_n should be increased until the value of its marginal product is exactly counterbalanced by its cost. The same is true for smoke: however, as long as no regulatory controls are in force, smoke can be generated without incurring costs, so that each firm would produce smoke up to the point where its marginal product is nil, i.e.:

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[1] The price system is relative to the numéraire good, taken to be p_N, which is normalized to one.

$$\frac{\delta E}{\delta s^E} = \frac{\delta M}{\delta s^M} = 0 \qquad <5>$$

The socially optimal solution to this problem would also require equalizing the marginal benefits of controlling smoke generation (mostly reduced damages) to the marginal costs of control of each firm. As before, when the gain in value just equals the expense, this optimal condition is met. This presumes we can evaluate damages from pollution as accurately as we can evaluate the cost of pollution control. In fact, this is a very tricky and somewhat subjective problem. Baumol and Oates (1971) offered a pragmatic solution to the problem, that involves fixing environmental quality targets (that may be varied from time to time) which could then be met at least cost[2].

Suppose that the government, using a strategy inspired by Baumol and Oates, implements a program of tradable permits, cutting total allowable emissions by half. It calculates emissions without controls, indicated by s^E_0 and s^M_0, and issues permits, so that, if D is the total number of permits:

$$D = \tfrac{1}{2}\,(s^E_0 + s^M_0) \qquad <6>$$

Since the firms employ different production technologies, it is improbable that condition <5> could be met if each firm cut its emissions by exactly half. The permits will have a positive price, p_s, and <5> now takes a form similar to the other inputs defined in <4>:

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[2] A dynamic general equilibrium model that permits searching for the optimum may be found in Mallory (1990a).

$$P_s = \frac{\delta E}{\delta s^E} = \frac{\delta M}{\delta s^M} \qquad <7>$$

Besides permits, taxes or subsidies could also be used to achieve the efficiency conditions defined by <4> and <7>. Permits have a number of important advantages over alternative mechanisms, which has led to gradually increasing interest in this approach in the context of environmental problems[3], namely:

- potentially destabilizing entry conditions do not exist, as new entrants would have to acquire someone else's permits;
- it is a less "noisy" signal when the true form of marginal cost of control and damage functions is uncertain;
- it maintains environmental quality at a specified level; and
- it accomodates new firms and growth of existing firms.[4]

2 A NUMERICAL EXAMPLE

A numerical example will show how firms' interests diverge on the question of the initial distribution. Moreover, the small number of participants breeds market power which can vitiate most of the efficiency gains expected from economic mechanisms.

Each firm's demand for SO_2 emissions as an input can be derived directly from the profit function using Hotelling's Lemma. Using π as the profit function, this demand may be expressed as:

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[3] It is also, of course, the system which appears to be favoured in the United States. cf. United States of America, (1989), "A Bill to Amend the Clean Air Act ...", which as of this writing had passed in different versions in the House and Senate and had gone to conference.

[4] These are more fully discussed in Mallory (1990b).

$$s^E = \frac{-\delta\pi^E(p)}{\delta p_s} \quad \text{and} \quad s^M = \frac{-\delta\pi^M(p)}{\delta p_s} \qquad <8>$$

Even if all other prices remain constant, outputs of the two firms may vary in response to changing permit prices. We will posit linear demand functions for smoke of the form:

Firm E $s^E = 11\ (8 - p_s)$ <9>

Firm M $s^M = 88\ (1 - p_s/3)$ <10>

We can find the price for permits by solving <9> and <10> for p_s and equalizing the results:

$$3 - 3/88\ s^E = 8 - 1/11\ s^M \qquad <11>$$

In that total pollution is to be reduced by half, solving gives:

$$s^E = 24 \qquad \text{and} \qquad s^M = 64 \qquad <12>$$

The equilibrium price of the permits is 2.18 (dollars) at the efficient allocation.

Emission permits may be distributed free or they may be sold; there are numerous intermediate possibilities as well. Free distribution has been justified on the basis of acquired rights to the emissions through historical use, or that the whole of society should pay for changes necessitated by evolving social objectives.

The distributive impact of different régimes emerges both with regard to the cost of pollution control and the cost of permits. Selling the permits by auction raises revenue at the

Table 1

Total Expenses to Firms with Distribution by Auction

	Pollution Control	Cost of Permits	Total
Firm E	69.8	52.4	112.2
Firm M	26.2	139.6	165.8
Total	96.0	192.0	288.0

expense of the polluting firms: this cost is shown for the two hypothetical firms E and N in Table 1. Depending on the shape of the control cost curves and the number of permits available, permit costs may be more or less than the pollution control cost itself. In this example the total cost of permits exceeds total expenses on pollution control, but this need not be so.[5]

2.1 FREE DISTRIBUTION AND DUOPOLY BARGAINING

Granting pollution rights to the firm can be seen as a form of subsidy: whoever gets more permits is the recipient of a larger grant. Yet a variety of different schemes can be described as "equitable", including equi-absolute or equi-proportional reductions in emissions, based on either their original or current values, or equi-marginal cost, to name a few. The last named characterizes a least cost mechanism, while C&C regulations more often focus on emissions.

While different "give away" schemes can have dramatically different effects on individual firms, "the literature provides very little guidance on the consequences of choosing among these various options" (Atkinson and Tietenberg, 1984, p.149). Nevertheless, the government must decide to whom to give the permits. Firms may endeavour to promote the rule that favours them most. Maloney and McCormick (1982) go so far as to say that "at least some firms always benefit from regulation" (at least if they are not being charged for the permits).

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[5] This observation is supported by simulations run by Palmer, Mooz, Quinn and Wolf (1980), Lyon (1982), Hahn and Noll (1983), and Atkinson and Tietenberg (1984).

The strategic interest of firms can be examined in more detail by comparing control expenditures under the "efficient" solution to some other allocation, such as an equal distribution (44 each). The government would in fact have great difficulty determining the efficient allocation a priori.[9] The firms would have incentive to trade in order to reduce their pollution control expenses. The burden of controlling pollution shifts heavily between the two regimes, showing that the firms are likely to have quite different ideas on which regime is better.

Table 2

Pollution Control Expenses under Different Allocation Regimes

	"Efficient"	Equal
Firm E	69.8	33.0
Firm M	26.2	88.0
Total	96.0	121.0

Firm E may not wish to sell to M, even though it has a financial incentive to do so. Three possible reasons can be given: a large producer might be able to prevent a competitor from locating nearby; a firm might hold on to unused permits anticipating later growth; or, the permit holding company may simply be too preoccupied with other matters to liberate emission permits for the use of others. Thus, any outcome could be considered an equilibrium. Since most acid rain emissions in Canada come from a few sources, the possible concentration of market power in the hands of one or a few firms is a matter of considerable concern.

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[9] Hahn and Noll (1982) argue against attempting to implement the efficient solution as it would result in a thin market.

Thus the problem is not as simple as deciding whether SO_2 generators have acquired rights or not: no regulatory scheme, whether by "command and control", permits, or whatever, can avoid the question of distributional impact on firms. This question emerges more clearly under a permit scheme because the government, having created the permits, has the power to make an initial distribution according to a rule of its choice. The actual costs of control also vary according to the control targets that are set, and this burden is also determined de facto by the government.

When large polluters already held the permits in perpetuity, the efficiency characteristics of the method are jeopardized, and the extent to which these rights are attenuated, the difficulties are reduced. Roberts (1982) argues strongly for permits that "depreciate", that is, are valid for a period of years, after which they expire and must be purchased. Such a method makes it much more likely that the division among firms will ultimately be efficient. Clearly, the sale of permits is less likely to be favoured by industry. As Dewees puts it, "[i]f the political process responds to interest groups that are strongly affected by a policy, the effluent charge and the sale of effluent rights are in deep political trouble unless the revenues are used to compensate the losers."

3 PROVINCIAL JURISDICTION AND REGIONAL INCIDENCE

The limited role that the federal government has defined for itself in environmental problems, and sulphur oxide emissions in particular, relies on its authority to implement international obligations.[10] This was invoked as the justification for the Clean Air Act amendments of 1980, which give it the right to impose a national standard for sulphur oxide emissions. (Whether it will ever do this is another matter.) The federal government has focussed its efforts on conciliating the competing interests of the provinces concerning acid emissions. Thus, in 1987 and 1988 it signed a series of ententes with the seven easternmost provinces, by which they undertake to implement specific cuts in emissions by 1994 (except for Quebec, which gave itself a deadline of 1990).

Transboundary effects can be very significant, and so should be taken into account. Two spatially separate sources will not have the same environmental impact (per unit of emission) as measured at air quality sampling stations, thus one-for-one trades between the firms would not achieve economic efficiency. The direction and turbulence of the winds play a large role, as does the relative concentration of the sources.

Permits may be based either on emissions, usually referred to as an **Emission Permit System** (EPS), or on the impact of the emissions on environmental parameters, generally known as **Ambient Permit Systems** (APS).[11] The former type assumes that all emissions have at least approximately equivalent impacts on surrounding areas, and emissions are redistributed through trades focusing only on lower cost methods of emission control.

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[10] cf. Nemetz, 1986.

[11] Montgomery (1972) formalised this distinction.

To take spatial location into account, AP trading systems compensate for changes in air quality through transfer coefficients. There are one hundred and fifty monitoring stations in Eastern Canada. For each receptor there would be a separate market, and permits must be held by each source for every receptor site they affect. The problem would be very complex, and it might be impossible to organize any trades at all.

However, when sources are close together, zones can be used to group sources. Using a system of zones, one-for-one emission based trades could be made between sources within a zone. Such a system is a hybrid of the EPS and APS models. In Canada, depostion rates vary much less within individual provinces than across the whole country. Thus provinces (possibly subdivided) might be considered appropriate divisions for zones. This approach dovetails neatly with the extensive jurisdiction that the provinces have. There would be no stringent need for the rules in each province to be identical.

The incentive to trade between zones would emerge with any disparity in permit prices between the two. Trades between zones are tantamount to varying emission ceilings, so that this would involve altering the ceilings that have been established. The terms of trade should be determined by the transfer coefficients, which allow for the difference in deposition rates that sources in each zone are expected to produce. Allowing such inter-zone trades could bring about substantial cost savings without negative impacts on the environment.

4 CONCLUSION

It is often remarked that firms would prefer programmes where permits are given away rather than sold, but differences in firms' cost structures will contribute to different preferences for regulatory intervention. Where market concentration is likely to occur, "give away" permit schemes are not likely to meet the economic objectives that are the *raison d'être* of such a program. Auctioning the permits would not be affected by this problem, but would likely encounter more determined resistance from industry.

The problems associated with regional diversity appear to be less thorny. Grouping emitters that are close together is not just a simplifying assumption, but one that respects the importance of provincial jurisdiction.

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E3

ESTIMATING PUBLIC BENEFITS OF IMPLEMENTING THE PROPOSED REVISIONS TO REGULATION 308

Erik Haites, Barakat & Chamberlin and Patricia Blyth, Ministy of the Environment

BACKGROUND

The Ministry of the Environment published a discussion paper on air pollution regulation in Ontario in November, 1987.[1] That document identified problem areas with the existing air pollution legislation and regulations. It went on to propose reforms that would impose direct emission limits on all air pollution sources of any appreciable size. As part of the review process for the proposed revisions to Regulation 308, the Ministry of the Environment commissioned four closely related studies to examine different aspects of these proposed changes.

This study identified the expected air quality, health and environmental benefits to the public from implementation of proposed revisions to Regulation 308. Where possible, these benefits were quantified and valued in economic terms. The study covered 96 contaminants emitted by over 3,500 establishments in 48 industries across Ontario. Benefits were estimated under five scenarios for implementation of the proposed revisions.

ANALYTICAL FRAMEWORK

The study was an ambitious attempt to grapple with a problem at the frontiers of industrial chemistry, health risk analysis and economics. The public benefits of reduced contaminant emissions depend upon:

- the contaminant whose emissions are reduced;
- the change in concentration of that contaminant at each point;
- the population and environmental resources in the areas where concentrations are reduced; and
- the human health and environmental responses to the reduced concentrations.

Figure 1 illustrates the problem of identifying and estimating benefits. It shows a source of contaminant emissions that would be affected by the proposed revisions. For most contaminants there are other sources that would not be affected by Regulation 308. These include motor vehicles, forests (a major source of some types of hydrocarbon gases), point sources governed by other regulations, sources too small to be affected by Regulation 308 and emissions that come from outside the province.

The proposed revisions to Regulation 308 would reduce the emissions from specified courses, and this would reduce the ambient concentration in the area surrounding the

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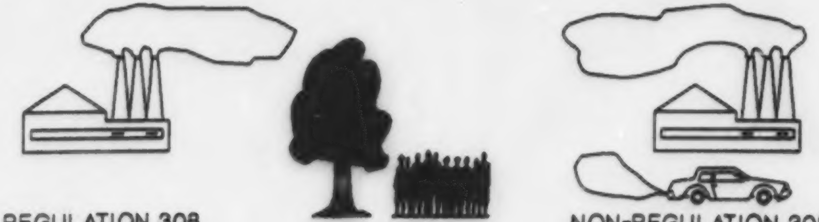
[1] Clean Air Program, Stopping Air Pollution At Its Source, Discussion Paper, Air Pollution-General Regulation, (Regulation 308), Ministry of the Environment, November 1987.

THE ANALYTICAL PROBLEM



REGULATION 308
CONTAMINANT
EMISSIONS

RESOURCES

NON-REGULATION 308
CONTAMINANT
EMISSIONS

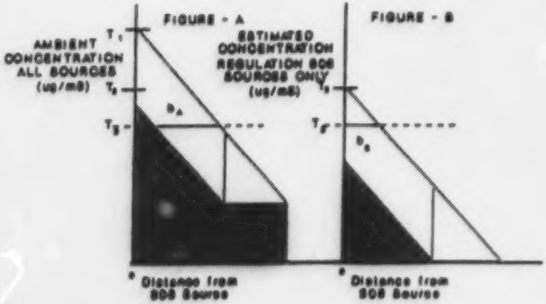


FIGURE - A
FIGURE - B
AMBIENT CONCENTRATION ALL SOURCES (ug/m3)
ESTIMATED CONCENTRATION REGULATION 308 SOURCES ONLY (ug/m3)
T_1
T_2
T_3
T_s
T_E
D_A
D_B
0
Distance from 308 Source
0
Distance from 308 Source

LEGEND:

- ■ - Present Concentration Non 308 Sources
- ■ - Proposed 308 Source Concentration
- □ - Reduction in 308 Source Concentration

source, assuming that emissions from other sources did not change. The change in ambient concentration can be estimated from the change in emissions from Regulation 308 sources. However, the level of ambient concentration of a given contaminant cannot be determined without knowing the emissions from all non-Regulation 308 sources. These emissions are usually not known.

EMISSIONS SOURCES

A list of economic sectors suspected to emit one or more of the 96 Regulation 308 contaminants was developed in consultation with the Ministry of the Environment and the consultants responsible for the related studies. The starting point was the activities or processes, such as whey drying, painting of automobiles, or incineration of hospital wastes, believed to generate one or more of the contaminants of interest. The activities and processes of interest were linked to SIC Standard Industrial Classification categories so that he technical and economic information collected and organized on that basis could be used. In many cases the correspondence was very good, in other sectors the analysis was limited to part of an SIC industry; and in a few cases, such as hospital, municipal and industrial incinerators, we simply defined the sector to suit our purposes.

We used two principal sources to identify locations and sizes of establishments in each sector. These sources are:

- the Made in Ontario data base compiled by the Ontario Ministry of Industry, Trade and Technology; and
- a listing of establishments purchased from Statistics Canada.

EMMISSIONS BY SOURCE

The emissions data were supplied by Senes Consultants Ltd. They provided estimated annual emissions by contaminant for each economic sector under the present regulations and under the five scenarios for implementation of the proposed revisions to Regulation 308. We adjusted these data in several ways to meet the needs of our analysis:

- the emissions had to be apportioned among the individual sources in the sector;
- the capacity utilization assumed had to be changed;
- the emissions rate had to be changed from tons per year to grams per second; and
- the composite categories of PM and VOC's had to be disaggregated into their constituent chemicals.

Total emissions for the sector were apportioned among the individual establishments in the sector on the basis of the selected measure of size, usually employment. The emissions were adjusted to reflect capacity utilization. Senes estimated emissions at full capacity, but benefits occur only as a result of changes to actual emissions. Hence, emissions were scaled to actual capacity utilization for the industry. Finally, the emisions rate was converted from tonnes per year to grams per second assuming continuous operation.

rate was converted from tonnes per year to grams per second assuming continuous operation.

One of the challenges in this project was to disaggregate PM and VOC's emissions into their individual chemical constituents. Reduced emissions of particulate matter, regardless of the composition, can yield health (respiratory problems, eye irritations etc.) and other (soiling, visibility reduction) benefits. But most health and environmental benefits derived from reduced emissions of PM's and VOC's result from lower concentrations of specific chemicals. Thus, the composition of the VOC and PM emissions had to be determined so that the changes in emissions of specific chemicals can be examined. This was done using U.S. data on the composition of PM and VOC emissions for various processes.

DISPERSION MODELLING

When a contaminant is emitted by a source, it is dispersed over the surrounding area. A dispersion model was used to calculate annual average ambient concentration attributable to the emissions from each source. The Ministry of the Environment's new dispersion models developed for use with Regulation 308 were used for the analysis. These models cover an area 24 km in each direction from the source.

We used a "pre-public-release" version of the Ministry's GAS model for the dispersion modelling. The climatological data it requires as input include both surface observations and upper air observations. There is no single station in the southern part of Ontario that has all of the information needed. On the basis of similarity of weather conditions and proximity to Regulation 308 emission sources, fourteen Ontario weather stations were selected to represent weather conditions across the province. A representative year was identified, U.S. or Quebec upper air observations were matched to each station and the dispersion pattern calculated for each of these fourteen stations.

To precisely model emissions from such sources the exact dimensions of the building and the stack must be known. For this study, no information was available on building or stack dimensions for any source. To estimate ambient concentration, each source was assumed to be a building of 7 m height and 100 m width with a stack of less than 14 m elevation, emitting pollutants at 0 velocity and at ambient exit temperature. Such a building is a typical "industrial park" source.

Subsequently, the simplifying assumption that all stack characteristics were similar was dropped. Instead, for each industry detailed stack characteristics and emissions data for a stratified sample of establishments were applied to the industry as a whole. The resulting emissions data were then used to re-estimate the total benefits associated with revisions to Regulation 308.

AMBIENT CONCENTRATIONS

Many of the contaminants studied are also emitted by sources other than the specified industries. To calculate benefits it is sometimes necessary to know the change in the ambient concentration from all sources likely to occur as a result of implementation (in respect of some sources) of the proposed revisions to Regulation 308.

Of the 96 contaminants considered, monitoring data are available only for cadmium, chromium, lead, manganese, nickel, sulphur dioxide, PM and total VOC's. The monitoring data are point data, i.e., ambient concentrations at the monitoring station locations. Using the dispersion modelling results, we determined the concentration of a monitored contaminant from Regulation 308 sources at each monitoring station. We subtracted this concentration due to Regulation 308 sources from the ambient concentration at the monitoring station. The result was a "residual" value for ambient concentration of the contaminant due to non- Regulation 308 sources at each monitoring station.

Not surprisingly, this subtraction did not lead to uniform "residual" figures at all monitoring stations. For each contaminant, except sulphur dioxide, we added the maximum "residual" value from all monitoring stations to the estimated concentration due to emission from Regulation 308 sources. This maximum residual was added to the concentration due to Regulation 308 source emissions under existing regulations, and under each implementation scenario for the proposed revisions to Regulation 308. The result was an upper bound estimate of total ambient concentration of the contaminant at all relevant points.

EXPOSURE - RESPONSE FUNCTIONS

The relationship between the exposure to a contaminant and the consequent damage is called an exposure-response function. Profiles were assembled for each contaminant, summarizing known effects, relevant standards and exposure-response functions where available.

Exposure-response functions were identified for carcinogenic or suspected carcinogenic contaminants. Functions were also available for some non-carcinogenic contaminants which have effects on health; nitrogen dioxide, sulphur dioxide and particulate matter. Functions for visibility effects and damage to materials were available for nitrogen dioxide and particulate matter.

It should be noted that the absence of an exposure-response function does not mean that health or other effects will not occur, only that their magnitude cannot be estimated at present. Furthermore, it should be recognized that the approach taken to benefit estimation, based on measurable benefits within a single year, did not allow for damages resulting from the bio-accumulation of toxic chemicals.

RESULTS

Some of the principal known sources of damage to other environmental resources, such as ozone, nitrogen dioxide and sulfates play a relatively minor role in this assessment. The largest sources of nitrogen dioxide and sulphate emissions fall under the acid rain initiative and hence outside the purview of this analysis. Ozone was not addressed in this study either, because it is formed in the atmosphere rather than emitted.

Cancer Mortality

Many of the 96 contaminants analyzed are suspected, probable or known carcinogens. Cancer unit risk factors are available for 20 of those contaminants. These enabled estimates to be made of the reduced risk to cancer mortality resulting from the proposed revisions to Regulation 308, as shown in Table 1. A reduction in death due to cancer of ten to seventeen people per year can be expected from reduced exposure to arsenic, chromium and nickel. Reduced exposure to other cancer causing contaminants were found to be insignificant with respect to mortality.

Non-Cancer Mortality

Exposure-response functions for estimating the reduction in non-cancer deaths resulting from lower contaminant emissions are available for sulphur dioxide and particulate matter only. The estimated reductions are shown in Table 1. The reduction in non-cancer mortality is roughly four times the reduction in cancer mortality.

Table 1 Estimated Reduction in Annual Mortality by Contaminant and Scenario

	A & D	B	C	E (to 2003)
Cancer				
1,3 Butadiene	1.0	1.0	1.0	1.0
Arsenic	7.0	8.0	6.0	7.0
Chromium	8.0	8.0	4.0	8.0
Nickel	0.5	0.5		0.5
Subtotal Cancer	17	18	11	17
Non-Cancer				
Sulphur dioxide	56	70	19	19
Particulate matter	11	12	5	8
Subtotal non-cancer	67	82	24	27
Total Reduced Mortality	84	100	35	44
Estimated Value (million 1986 $C)				
low	$184.8	$220.0	$77.0	$96.8
central	$583.8	$695.0	$243.3	$305.8

Source DPA (1988, 1989)

Reduced Morbidity

Exposure-response functions for health benefits due to reduced morbidity are available for sulphur dioxide and particulate matter. The estimated human health benefits resulting from reduced emissions of these contaminants are shown in Table 2.

Table 2: Estimated Reduction in Annual Morbidity by Contaminant and Scenario

	A & D	B	C	E
Sulphur Dioxide				
Hospital admissions for respiratory disease	136	171	45	47
Hospital days for respiratory conditions	1,341	1,686	448	460
Value (million 1986 $C)				
low	$0.9	$1.2	$0.3	$0.3
central	$3.1	$3.9	$1.0	$1.1
Particulate Matter				
Emergency room visits	637	681	321	492
Restricted activity days	133,500	142,500	67,000	103,000
Value (million 1986 $C)				
low	$1.4	$1.5	$0.7	$1.1
central	$8.2	$8.7	$4.1	$6.3
Total (million 1986 $C)				
low	$2.3	$2.7	$1.0	$1.4
central	$11.3	$12.6	$5.1	$7.4

The benefits from reduced sulphur dioxide emissions consist of reductions in hospital admissions and the number of hospital days for respiratory conditions. Benefits from reduced particulate matter emissions consist of reductions in emergency room visits and restricted activity days.

Reduced Exposures to Concentrations Above the Proposed Standards

The estimates of human health benefits summarized in Tables 1 and 2 only capture a part of the human health benefits from more stringent control emissions required to meet the proposed revisions to Regulation 308. Exposure-response functions have yet to be developed for the majority of contaminants examined.

In the absence of an exposure-response function, the analysis examined the population exposed to contaminant concentrations above the standard included in the proposed revisions. In the case of cadmium, chromium, lead, nickel and sulphur dioxide, where monitoring information was available, the analysis was based on the estimated ambient concentration (from all sources). For the other contaminants, however, the analysis was limited to exposure to the concentrations estimated from Regulation 308 source emissions alone. In those cases, they underestimate the public benefits of the proposed revisions to Regulation 308.

Table 3 summarises the estimates of population exposed to concentrations of contaminants above the proposed ambient standards. Eleven contaminants were estimated to be at above-standard levels at the estimated emission levels in 1987. The revisions to Regulation 308 under all scenarios would significantly reduce the population exposed to concentration levels above the proposed standards.

The analysis was based on annual average concentrations, the dispersion of these contaminants was been modelled on the assumption that they are gases, and the smallest area considered was 16 km^2. Hence the analysis did not detect concentrations above the proposed standard if they occur in smaller areas, especially near the emission sources, or over shorter periods.

Materials Damage

Functions for estimating reduced damage to materials are available for nitrogen oxides and particulate matter. These functions are expressed in terms of the dollar value of materials damage per unit change in ambient concentrations. Consequently, they cannot be used to estimate the reduction in damage measured in physical units, such as the reduced frequency for painting or the increased longevity of materials. Table 4 shows that the estimated benefits from reduced damage to materials are mostly attributable to the reduction in nitrogen oxides.

Visibility Benefits

As with the reduction in materials damage, the functions available for estimating the value of improved visibility are expressed directly in dollar terms and do not permit benefit estimates to be made in physical units. These functions, which were derived from

Table 3 Estimated Population Exposed to Above-Threshold Concentrations of Contaminants (000's)

	Current	Scenarios A & D	Scenario B	Scenario C	Scenario E
Arsenic	228	34	34	67	34
Cadmium*	**	-	-	-	-
Chromium*	75	26	26	34	26
Ethylene Dibromide	345	-	-	-	345
Fluorides	**	-	-	-	-
Lead*	12	-	-	-	-
Nickel*	34	-	-	-	-
Nitrogen Oxides	1	1	1	1	1
Silica	645	129	83	288	238
Sulphur Dioxide	67	**	**	12	12
Suspended Particulates	159	22	**	95	45

Notes:

* Denotes contaminant for which population exposure is based on ambient concentration from all sources. In all other cases exposure is to concentrations due to Regulation 308 Source emissions alone.

** Population exposed is less than 500.

- Exposure levels are negligible.

studies of the value of changes in visibility in California, yield extremely high estimates for the value of improved visibility when applied to the emission reductions considered in this assessment. These high values are due, in part, to the inability of the exposure-response function to distinguish between proportionately large improvements in areas where existing visibility is low, and those where visibility is relatively high. In the latter case, observed visibility increases due to reductions in particulate emissions could be very small, yet would be given the same monetary value as equal percentage reductions in areas where visibility is originally very poor. For this reason the benefits were omitted from the report.

Odour

Five of the 96 contaminants and emissions from restaurants are considered to be potential odour problems. This assessment indicates that hydrogen sulphide, trichloroethylene and restaurants all satisfy the standards proposed as part of the revisions to Regulation 308.

Phytotoxicity

Only eight of the 96 contaminants were identified as being potentially harmful to plants: cadmium, chlorine, ethylene, hydrogen chloriden, nickel, selenium, and sulphur dioxide.

At present only very small areas are exposed to concentrations in excess of the proposed standards for these contaminants. Hence, the public benefits in the form of reduced damage to crops and forests resulting from the proposed revisions are negligible.

AGGREGATE ECONOMIC VALUATION

The estimated value of reduced mortality and morbidity and of less damage to materials resulting from implementation of the proposed revisions are summarized in Table 5.

These figures apply only to those few cases where the public benefits can be quantified and the associated economic value can be estimated. The absence of a damage function or even emissions data for a contaminant does not mean that there is no benefit to be had by regulating emissions of that contaminant. Given the limited range of contaminants and benefits that can be quantified and valued, the figures in Table 5 should be considered minimum estimates of benefits.

Annual benefits range from $300 to $625 million (1986 C$) in the low case and from $725 to $1,525 million in the central case. Health benefits account for 25 to 35 percent of the total in the low case and 35 to 45 percent of the total in the central case. The least stringent scenario (C) yields the lowest benefits and the most stringent (B) produces the highest benefits.

REVISED PROPOSALS

Revised proposals to reform to Ontario Regulation 308 under the Environmental Protection Act were issued for comment on August 16, the proposals are the centrepiece

Table 4: Estimates of Benefits From Reduced Damages to Materials by Scenario (million 1986 $C)

	A & D	B	C	E
Nitrogen oxides				
Low	$333.2	$402.9	$234.7	$279.7
Central	$666.3	$805.8	$468.8	$559.4
Particulate matter				
Low	$1	$1	$1	$1
Central	$18	$19	$9	$14
Total				
Low	$334.2	$403.9	$235.7	$280.7
Central	$684.3	$824.8	$477.8	$573.4

Table 5: Aggregate Amounts of Benefits to Which an Economic Value Has Been Assigned (Millions of 1986 $C Annually)

	A & D	B	C	E
Low Cost				
Reduced mortality	$184.8	$220.0	$77.0	$96.8
Reduced morbidity	$2.3	$2.7	$1.0	$1.4
Lower materials damage	$334.2	$403.9	$235.7	$280.7
Total	$521.3	$626.6	$313.7	$378.2
Central Case				
Reduced mortality	$583.8	$695.0	$243.3	$305.8
Reduced morbidity	$11.3	$12.6	$5.1	$7.4
Lower materials damage	$684.3	$824.8	$477.8	$573.4
Total	$1,279.4	$1,532.4	$726.2	$886.6

of the province's Clean Air Program, designed to reduce atmospheric emissions from stationary sources. The requirements will affect an estimated 20,000 emitters. The draft regulation requires:

- that all significant stationary sources of emissions to the atmosphere to be controlled to minimize releases to the environment;
- controls commensurate with the known or suspected hazard of the contaminant being emitted, with the strictest controls on emitters of substances known to have serious health and environmental effects (toxics), especially those which persist, accumulate in living things and have the ability to cause cancer or mutate genes;
- that all significant (new and existing) sources of emissions to the atmosphere must have a certificate of approval, renewable on a ten-year basis, to operate; and
- that community air standards be met throughout the province.

To achieve these aims the Clean Air Program proposes:

- systems for classifying contaminants according to their potential to impact the environment;
- a three-level system of emission control requirements which will be linked to the classification system to ensure appropriate controls;
- requirements for Certificates of Approval to construct and operate, with the operational part renewable every ten years;
- provisions to require the use of state-of-the-art computer models or their equivalent to estimate the impact of proposed emissions on existing community air quality;
- a process for reviewing the current single source point of impingement standards and converting them to ambient air standards, and to produce new standards as the need arises;
- revisions to the existing procedures concerning the granting of air approvals;
- a phasing-in mechanism based on the contaminant evaluation scheme;
- monitoring and quality assurance requirements.

A six-month comment period has been established for the regulatory proposal.

E4

Recycling, Reducing and Reusing: A Theoretical Framework

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1.0 INTRODUCTION

Macroeconomic models are generally based on a particular national income accounting framework. The current approach treats waste and pollution generation in such a way that any increase in these activities increases directly the GDP of the economy. Thus, a society can increase its GDP by simply inceasing the waste it produces. This follows from the fact that pollution abatement and sewage treatment activities appear as part of the final demand of the economy. Carbage collection and sewage treatment are part of the municipal government sector and this sector, like all other government activity, is treated as if it produces final output. Common sense suggests that no society should be considered richer or better off if it were to produce more waste. Since the current GDP measure does exactly this, it appears sensible to re-examine the GDP concept and the way it is measured.

In this study we present a suggested reformulation of the accounting framework so as to treat waste management and pollution abatement as services to business whose costs should be charged against business revenues. Even such services to households may be considered as costs of output to the extent that part of household activity may be incorporated within the business sector. In this way they appear as a cost to society and not as final output.

The major contribution of the study, however, is the new theoretical framework that is developed to correspond to the new reformulated accounting framework. Within this new framework it is possible to identify clearly and carefully the recycling activity and the operations of waste management. The rectangular input output framework is particularly suited for this treatment as it allows different industries to produce the same output, and identifies different commodities as inputs in the production of the same output. In this way paper can be made from virgin pulp or from recycled paper. The two industries use different technologies but produce the same output. Several new commodities are also introduced into the system. These include recyclables and recycled commodities. What in the past was waste and disposed of is now a new input into the production of consumables. Recyclables are produced primarily but not exclusively by households and institutions, and are used by the recycling industry to produce products that are almost indistinguishable from virgin products.

The new framework extends our ability to deal with environmental and waste management issues that are dificult or impossible to deal with within the old framework. The " throwaway society" such as the one we have in Canada produces about 1.7 kgs per person per day. This is the highest per capita waste production in the world. Ontario alone produced about ten million tonnes of waste in 1987, this is more than one tonne for every person. Waste volumes are increasing at very rapid rates. Over the past decade the per capita waste generation rate exceeded 25 percent. As a result, landfill sites in high growth areas such as Metro Toronto have experienced bottlenecks. Over 160 landfills in the province have less than two years of approved remaining capacity.

With the new framework, it is possible to examine the socioeconomic consequences of increased use and production of recyclables. Equally important is our ability to assess the relative efficiency of alternative policies to reuse or reduce the use of products and resources through price incentives and full cost charges.

2.0 The Model

Recycling, reusing and waste management activities involve the use of scarce resources and the generation of outputs and services. Typically, these activities were either neglected, misallocated or subsumed within other activities of other sectors within the standard input output accounting framework. Any attempt to focus on these activities calls for a major reformulation of the standard accounting framework. The adjustment process involves not only broadening the use, make and final demand matrices of the rectangular input output framework to encompass new commodities and industries, it also calls for redefining of the accounting relationships governing the system.

2.1 The Modified Use Matrix

The standard use matix is extended to include explicitly sorting station activities, recycling and waste disposal activities. These industries use resources and generate value added. The commodity set is also expanded and disaggregated to show explicitly scrap, recyclables, recycled products and waste treatment and disposal services. Table 1 presents the modified structure of the use and final demand matrices that reflect the expanded indutry and commodity spaces.

Table 1

The Modified Use and Final Demand System

Industries Commodities	1	2	S	R	W	H	G	E	M	Q
Composite 1	U_{11}	U_{12}	U_1S	U_RR	U_1W	H_1	G_1	E_1	$-M_1$	q_1
Paper 2	U_{21}	U_{22}	U_2S	U_2R	U_2W	H_2	G_2	E_2	$-M_2$	q_2
Recyclable paper 3	0	0	U_3S	U_3R	U_3W	H_3	G_3	E_3	$-M_3$	q_3
Recyclable composite 4	0	0	U_4S	U_4R	U_4W	H_4	G_4	E_4	$-M_4$	q_4
Scrap 5	U_{51}	0	U_5S	U_5R	U_5W	H_5	G_5	E_5	$-M_5$	q_5
Waste Management 6	U_{61}	U_{62}	U_6S	U_6R	0	H_6	G_6	E_6	$-M_6$	q_6
Recycled Products 7	0	U_{72}	0	0	U_7W	0	0	E_7	$-M_7$	q_7
Value Added	VA_1	VA_2	VA_S	VA_R	VA_W	VA_H	VA_G			Y
Gross Output Y+δg	q_1	q_2	q_S	q_R	q^W	H	G	E	-M	

A number of interesting characteristics are embedded within Table 1 that reveal the nature of the modifications suggested.

First, a strong distinction is made between recyclables and recycled products. Recyclables are gathered, sorted and delivered either to the primary industries or to the recycling industry.

Second, recycled products are either delivered as outputs to final demand or as inputs to primary industries.

Third, waste disposal services are allocated to businesses and to households. Deliveries to businesses appear as deliveries to intermediate demand. In the standard input output system waste disposal services are allocated entirely to final demand. This reallocation implies reducing the value of net output of the economy. In addition, charges paid by businesses for waste disposal services reduces their operating surplus and therefore the value added assigned to them. These charges appear as revenues of the waste disposal industry and raises its value added. Thus, two changes result from this adjustment. Net output of the economy is changed by moving a part of the deliveries of this activity from final demand to intermediate demand, and also the distribution of value added between industries.

2.2 The Modified Final Demand Matrix

Exporting and importing recyclables, recycled products and waste are allowed explicitly into the framework. Maintaining balance between supply and demand for these products is likely to be difficult particularly in the initial stages of production. Thus imports and exports of surpluses and short falls are likely to play prominent roles in sustaining the operations of these activities. Furthermore, final demand sectors are users as well as producers of recycled and recyclables. Their activities and choices will influence in a significant way the operations and activity levels of these sectors.

2.3 The Modified Make Matrix

The extension and expansion of the use matrix impose several modifications to the make matrix. Some of these changes include:

First, recyclables are primarily produced by all sectors including some final demand sectors.

Second, paper produced from virgin inputs is indistinguishable from paper produced from recycled paper.

Third, waste management services are produced solely by the waste management industries.

Fourth, recyclables are transformed into recycled products at sorting stations or at recycling industries.

Table 2

The Modified Make Matrix

Commodities Industries	1	2	R_P	R_C	R_S	6	7	Industries
1	V_{11}	0	V_{13}	V_{14}	V_{15}	0	0	g_1
2	0	V_{22}	V_{23}	V_{24}	V_{25}	0	0	g_2
S	0	0	0	0	0	0	V_{S7}	g_S
R	0	0	0	0	0	0	V_{R7}	g_R
W	0	0	0	0	0	V_{W6}	0	g_W
H	0	0	V_{H3}	V_{H4}	V_{H5}	0	0	g_H
G	0	0	V_{G3}	V_{G4}	V_{G5}	0	0	g_G
Commodities	q_1	q_2	q_3	q_4	q_5	q_6	q_7	8

Several features define the modification's to the structure of production presented in Table 2. They include: first, recyclables are produced by all sectors other than the sorting and recycling industries. Second, the paper industry produces paper from Virgin materials and recycled materials. Third, recyclables are transformed into recycled products by the sorting stations and the recycling industries. Fourth, households and governments are treated here as producing sectors of recyclables.

2.4 The Equations of the Model

The model has several components. We begin with the materaial balances: For i, we have

(1) $U_{i1} + U_{i2} + U_{iS} + U_{iR} + U_{iW} + H_i + G_i + E_i - M_i = q_i$

In more compact form

(2) $\underset{j}{\delta}\, u_{ij} - \underset{s}{\delta} l\ is = q_i$

$j = 1, 2, S, R, W$

$s = H, G, E$ and M.

when

l_{ij} : is the delivery of commodity i used in industry J.

l_{is} : is the delivery of commodity i with final demand category S.

The matrix defines the following relationships:

For Commodities:

(3) $q_1 = V_{11}$

(4) $q_2 = V_{22}$

(5) $q_3 = V_{13} + V_{23} + V_{H3} + V_{G3}$

(6) $q_4 = V_{14} + V_{24} + V_{H4} + V_{G4}$

(7) $q_5 = V_{15} + V_{25} + V_{H5} + V_{G5}$

(8) $q_6 = V_{W6}$

(9) $q_7 = V_{S7} + V_{R7}$

For Industries:

(10) $g_1 = V_{11} + V_{13} + V_{14} + V_{15}$

(11) $g_2 = V_{22} + V_{23} + V_{24} + V_{25}$

(12) $g_S = V^{S7}$

(13) $g_R = V_{R7}$

(14) $g_W = V_{W6}$

(15) $R_H + V_{H3} + V_{H4} + V_{H5}$

(16) $R_G + V_{G3} + V_{G4} + V_{G5}$

The Use matrix defines the following set of relationships

(17) $g_i = \sum_j uji + VA_i \qquad i = 1, 2, S, R, W$

and

(18) $H = H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + VA_H$

(19) $G = G_1 + G_2 + G_3 + G_4 + G_5 + G_6 + VA_G$

(20) $E = E_1 + E_2 + E_3 + E_4 + E_5 + E_6 + E_7$

(21) $M = M_1 + M_2 + M_3 + M_4 + M_5 + M_6 + M_7$

Equations (1) through (21) are accounting identities. The following hypotheses are tendered to operationalize the model.

(22) $\hat{I}_{ij} = \hat{I}_{ij}\, g_j \qquad j = 1, 2, S, R, W$

Commodity input use is proportional to industry output.

(23) $H_i = h_i\hat{H}$

Consumption by commodity depends on the proportion of labour income devoted to consumption.

(24) $\hat{H} = cLI$

Labour income is the sum of wages and salaries, "c" is the average propensity to consume.

(25) $G_i = g_iG$

Government expenditure by commodity is determined by constant shares "g_i".

(26) $E_i = E.$

Exports by commodity are determined exogenously.

(27) $M_i = m_i(M_i + q_i) \qquad i = 1, 2$

Commodity imports of the composite good and paper are proportional to total supply.

(28) $M_i = M_i$ $\quad i = S, R, W$

Other imports are exogenously determined.

(29) $V_{ji} = v_{ji} q_i$

The share of industry "j" is the production of commodity "i" as fixed by the existing market share coefficient v_{ji}.

Several additional restrictions on policy specifications may be postulated to simulate their effects on the economy's performance. For, example we may hypothesize the following:

(30)
$$H_4 + V_{H3} = S_H = H^H$$
$$H_4 = sh_4 S_H$$
$$VH_3 = sh_3 S_H$$
$$G_4 + V_{G3} = S_G = sgH$$
$$G_4 = sg_4 S_G$$
$$VG_3 = pg_3 S_G.$$

The parameters shi and sgi reflect the household and government recycling participation rates. Blue box programmes ultimately raise the values of these coefficients and allow model users to simulate the impact of such policies on waste disposal.

E-5

THE ECONOMIC IMPLICATIONS OF THE ZEBRA MUSSEL (*Dreissena polymorpha* Pallas) INVASION OF THE GREAT LAKES

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ABSTRACT

Various authorities and media reports have cited dollar values of the current or potential damages caused by the zebra mussel or of its control ranging from $3.7 billion to $5 billion for establishments on both sides of the Great Lakes over the next 10 years. The actual damages and adverse effects caused by the zebra mussel in Ontario and the monetary values and other economic implications associated with them are presented in this paper along with estimates of the monetary values of potential responses to the key adverse effects caused by the animal in Ontario and the potential economic implications of these consequences.

To date, at least 14 biofouling cases have been reported in Ontario. Capital and other one-time expenditures directly attributable to these cases amount to about $8.7 million. Ontario industrial establishments and power plants on the Great Lakes have so far been spared the extreme consequences of equipment damage and plant shut-downs. Potential costs of preventative measures in 8 Ontario Hydro power plants, 86 municipal water treatment plants and 67 industrial plants which use Great Lakes water directly amount to about $164 million for equipment and installations, $7.6 million per year for operating and chemical costs, $1.25 million each year for cleaning and removal and $2.25 million per year for monitoring activities. Ontario Hydro also intends to devote about $3.5 million in research over the next 3 years.

Application of an Ontario beach use model indicates that, in 10 beaches on Lake Erie currently infested with zebra mussels, beach use occasions could be reduced by as much as 18% if the effects caused by zebra mussels only partially reduced the attractiveness of the locations. However, if the adverse effects are perceived by people to be of major importance, beach attendance would be reduced by as much as 50%.

It is tentatively concluded that the consequences of the zebra mussel infestations and the costs incurred to respond to them will not cause undue economic or social repercussions so long as Great Lakes water users are vigilant and implement control or preventive measures in time. Increased monitoring and surveillance would be one of the best investments that can be made at this time.

1. INTRODUCTION

In only 2 years since it was first observed in Lake St. Clair, the zebra mussel (*Dreissena polymorpha* Pallas) has become a major problem for communities and industrial plants that line the shores of Lakes Ontario, Erie and Huron. A native of fresh water lakes in central Europe, larval forms of *Dreissena* were probably brought to the North America in the fresh water ballast of ships. Here in the Great Lakes, zebra mussels have found ideal conditions for reproduction, rapid growth, development of dense colonies (called *druses*) and wide dispersion.

Although individual mussels grow no larger that the size of a fingernail, they can cause serious biofouling in municipal and industrial water systems and unwholesome accumulations of shells on recreational beaches and shorelines. While all of the potential effects of the zebra mussel are not entirely detrimental, biofouling and other adverse consequences have dominated media reports.

Quantitative measures of the present and potential bio-physical impacts of the zebra mussel are of interest and importance to program development. However, the monetary values associated with these effects are needed to judge their importance to individuals and, with certain qualifications, to society as a whole. Value information is particularly important if both beneficial and adverse effects are involved. Estimation of the monetary values associated with a particular environmental problem or issue helps to determine how much money and effort ought to be allocated to a specific remediation activity such as zebra mussel control, clean-up and prevention of biofouling. Such estimates are also required in order to assess the broader economic implications that can result from these consequences.

Various authorities and media reports have cited dollar values of the current or potential damages caused by the zebra mussel or of its control. These values range from $3.7 billion for establishments on both sides of the Great Lakes over the next 10 years (Stanley, ca. 1990), "...$4 billion by the end of the decade... ...Billions more likely will be needed in the next century." (Grigson-Miller, Oct. 6, 1990) to $5 billion over the next decade (Toronto Star, Aug. 9, 1990). Attempts to verify and trace the sources of these estimates have revealed unclear methodologies, misquotes or lack of documentation.

Thus, while much valuable information about the biology of Dreissena polymorpha and the technologies of controls are being accumulated, little if any systematic work on the economic implications of the zebra mussel invasion of the Great Lakes is under way. The present study is intended to fill this apparent gap and assess the financial and economic ramifications of the zebra mussel in Ontario.

The primary purposes of this study are to:

1) present a documented accounting of the actual damages and adverse effects caused by the zebra mussel in Ontario and the monetary values and other economic implications associated with them, and

2) prepare documented estimates of the monetary values of potential responses to the key adverse effects caused by the zebra mussel in Ontario and the potential economic implications of these consequences.

2. PLAN OF PAPER

The present paper is a distillation of a more extensive reference report prepared by the authors (Dorman & MacKay, forthcoming). More details on each of the issues discussed here can be found in that reference.

In the next Section, steps and procedures that will be utilized to produce the relevant estimates are presented. This is followed in Section 4 by a brief description of the biological characteristics of the organism and an enumeration of potential effects on human structures and activities. Relevant data on the areas of current and potential infestation on the Canadian side of the Great Lakes are noted in this Section as well.

Methods and technologies which have been applied, and are being studied, to remove or prevent zebra mussel infestations are summarized in Section 5. Locations at which the zebra mussel has actually caused damages or has induced expenditures on clean-up or prevention are listed in Section 5. Estimates of the monetary values associated with different types of response activities (ie. cleaning of pipes vs preventative installations) in various sectors (eg. electric power generating stations, municipal water treatment) are presented in Section 6.

Potential effects of zebra mussel shell littering on recreational beaches are discussed in Section 7.

Section 8 reviews the experience and effects of other biological invaders of the Great Lakes, particularly the predatory sea lamprey (*Petromyzon marinus*).

Findings and conclusions are found in Section 9.

3. PROCEDURES AND METHODOLOGIES

An assessment of the economic implications of any environmental or natural resource phenomenon begins with information on the biophysical nature of the problem and the mechanisms by which human activities and perceptions are affected. When the relevant biophysical and human interrelationships are identified and quantified to the extent possible, data on the populations, resources, locations or facilities at risk must be assembled. These data are used to "scale up" the physical, spatial and economic dimensions of the effects in question.

A third step involves positing different scenarios that define potential human responses to the adverse (or beneficial) effects that are of concern. Human responses to the environmental issue at hand may involve the allocation of various types of natural and man-made resources to repair, replace or avoid adverse effects or they may involve the reduction in the utility and enjoyment of specific activities or natural assets because of the problem in question. Measures of these responses range from numbers of devices or process installed or chemicals and labour utilized to the change in the number of visits to, or the degree of enjoyment at, a recreational beach.

Monetary values provide a common unit, or numeraire, by which otherwise incommensurate commodities or biophysical consequences and measures can be aggregated together. Monetary values also indicate the relative importance of specific consequences or commodities to individuals and, under certain conditions, to society as a whole. Estimation of relevant monetary values using market price data or other methodologies is the fourth key step in the procedure.

The economic implications of an environmental problem or phenomenon extend beyond the dollar values of the direct consequences and effects. First of all, to the extent that costs of inputs to a large number of enterprises (or government operations) and production processes are increased, the market prices of relevant goods and services may be increased to recover these costs. If specific market conditions do not permit price increases, those firms incurring the cost increases will suffer reduced profits. These economic consequences would be regarded as adverse by consumers who pay higher prices or the shareholders of firms which incur reduced profits.

On the other hand, the increased expenses incurred by firms or agencies become increased revenues to supplier firms or increased employment and wage payments if the higher costs involve added staff time. Economic resources are not lost but redirected within the economy as a result of the issue at hand. Some sectors and firms experience gains as the demand for their goods and services expands.

To the extent that recreational activities such as swimming or fishing are adversely affected, values derived from market prices generally understate the values that people actually ascribe to these activities.

The social implications of a particular environmental concern may well transcend measurable economic effects if stocks of particular resources are depleted so that some groups or communities lose their livelihood or if price changes affect different groups or localities unevenly.

Proliferation of zebra mussel colonies has resulted in two key adverse links with human activities. First, there is the potential for biofouling and clogging of water systems to cause serious damages and financial losses in municipal water treatment plants, industrial facilities and power plants if left untreated. Second, accumulations of mussel shells on recreational beaches can reduce the attractiveness and utility of these resources to users.

Resources and effort must now be allocated to the removal of mussel infestations and to programs intended to prevent their accumulation in water systems. Moreover, authorities are searching for methods that could reduce zebra mussel populations in the Lakes, even before they begin infesting water intakes or other man-made structures. For each of these response actions, choices must be made as to the technologies or procedures to be applied and the level of effort to apply them. Comparisons of the costs of alternative response actions with each other and with the consequences of taking no action helps to make these choices.

First of all, the actual cases where zebra mussel damages, cleaning and removal or preventative actions have been taken in Ontario are documented.

Estimates of costs and the associated economic implications of the following responses to biofouling are examined in this paper:

a. no removal of mussel colonies or preventative actions are taken. This is a worst case situation.

b. mussels are removed and cleaned.

c. preventative actions are taken or systems installed.

d. monitoring and surveillance.

e. research, technology development and technology transfer.

Separate estimates of biofouling effects are prepared for three potential geographical ranges of the zebra mussel through out the Great Lakes: areas that are currently infested; the Great Lakes' shorelines of Ontario downstream from the infested areas; and all of the remaining shorelines of Ontario.

With regard to effects on beach use and enjoyment, estimates of the changes in beach visitation in areas that have recorded infestations of Dreissena are derived from a "beach use" model and data base prepared by Usher and Ellis (1987).

4. BIOLOGICAL CHARACTERISTICS, RANGE AND POTENTIAL EFFECTS

Dreissena polymorpha specimens were first identified in Lake St. Clair in June 1988. The animals found at that time were thought to be about 2 years old indicating that the original introduction probably took place during 1986 (Hart, July 1990). By May 1990, zebra mussels had been found at locations throughout the Great Lakes, from Cornwall on the St. Lawrence to Thunder Bay on Lake Superior. However, potentially troublesome colonies are so far found along Lake Erie shores, the Welland Canal and the Niagara River, Lake Ontario and Lake Michigan. Information on zebra mussel distribution throughout the Great Lakes is found in Griffiths, et al (1989).

A single female mussel can produce about 35,000 eggs each year during the summer and fall months when water temperatures rise above 12 degrees Celsius. The density of colonies or *druses* enhances successful fertilization and the production of thousands of free-swimming veliger *larvae*. The veligers can attach themselves to practically any horizontal surface where water flows are below 2.5 meters per second, including a docked ship. Ships with mussels and larvae attached have likely transported the animal to all parts of the Lakes.

Dreissena appears to have found virtually ideal environmental conditions in the lower Great Lakes and there are few natural predators of these organisms in North America. As a result, where mussel densities in Europe reach a maximum of 114,000 per square metre, colonies have been found to exceed 700,000 animals per square metre in Lake Erie (Griffiths et al., 1989). Adult mussels can survive anoxic conditions, exposure to air and extremely low water temperatures for many days, contributing further to the species' success in the Great Lakes.

Like all bivalve molluscs, Dreissena siphons water through its gills and removes microscopic phytoplankton as small as 0.7 microns in diameter. One adult zebra mussel filters about 1 litre of water each day and the filtering activity of thousands of mussels in a colony can noticeably increase the clarity of the surrounding water.

Dreissena's fecundity, mobility, small size and its propensity to colonize a wide range of substrates all contribute to its ability to cause biofouling in various types of water intake systems, presumably attracted by the flowing water that brings food within siphoning range. Europeans have contended with the zebra mussel for many decades. For example, as long ago as 1895, the Berlin water works were shut down because decaying mussels had contaminated the system (Griffiths et al., 1989).

In addition to clogging intake pipes and reducing water flows, the increased clarity brought about by zebra mussel filtering has resulted in increased algae and aquatic macrophytic growth near the Windsor water system intake. Decaying vegetation is apparently contributing offensive tastes and odours in the water that must be removed by costly carbon filtration.

Another concern related to biofouling, as yet unconfirmed, is the possibility that accelerated corrosion to metals could occur under the anoxic conditions of a dense mussel druse (Spencer, 1990).

Where colonies form near recreational beaches, piles of mussel shells up to three feet deep have accumulated which reduce the attractiveness of the beach and present hazards to bare-footed bathers (London Free Press, August 14, 1990).

In addition to these two well-publicized adverse effects, researchers have postulated a number of other characteristics and consequences which may be associated with zebra mussels.

a. the filtering actions of large colonies of mussels can increase the clarity of water. Increased clarity can be pleasing aesthetically but may have one or more of the following potential effects.

  - fish species that prefer turbid waters such as the walleyed pike (Stizostedion vitreum vitreum) will leave the area to seek more agreeable conditions.
  - phytoplankton, and the zooplankton that feed upon it, will be depleted by zebra mussels leaving little for fish and other aquatic organisms. The long-term consequences for Great Lakes' fisheries populations are uncertain at this time.
  - increased water clarity and light penetration allows the growth of benthic algae and aquatic plants. These plants can cause taste and odour problems in municipal water systems.
  - zebra mussels could be employed to remove excess nutrients and pesticides from natural waters. Press reports have claimed that the Russians are experimenting with Dreissena for such purposes (North Bay Nugget, June 15, 1990).

b. colonizing rocky areas that fish use for spawning may smother the fish eggs and crowd out spawning fish. On the other hand, smaller clusters of mussels can help to protect the fish eggs laid among them. The net effect is not yet determined.

c. while many freshwater molluscs serve as intermediate hosts of parasites in humans, Dreissena polymorpha has not been found to be heavily infected with such parasites. Continued surveillance is recommended to determine whether Dreissena becomes a vector for such parasites (O'Neill, 1989).

d. zebra mussels may also be used in biomonitoring studies because the organisms absorb contaminants which may then be analyzed (Alekseyev and Antipin, 1986 as quoted in Mackie et.al., July 1989).

e. zebra mussels may be a source of new pharmaceutical products and they have been used as calcium supplements in livestock feed in Europe.

The areas of Great Lakes shoreline that are most infested at this time extend from Windsor on the Detroit River through all of Lake Erie and include the Niagara River and Welland Canals. The Lake Ontario shoreline and the St. Lawrence River are currently at most risk of future problematic mussel infestations in Ontario. The St. Clair river and Lake Huron shoreline up to Kincardine is also currently viewed as at risk from colonizations that could cause biofouling or beach littering. The remaining Great Lakes shorelines and urban settlements on both sides of the border are at somewhat lower risk although those harbours with substantial shipping traffic would face proportionately higher risks of mussel infestation.

Authorities also fear invasions of inland waterways where thousands of home and cottage water systems could be at risk. This issue is, however, beyond the scope of the present investigation.

5. CURRENT DAMAGES, CONTROL MEASURES AND RESPONSES

There are, to date, at least 14 biofouling cases in Ontario where zebra mussel infestations have caused damages or have required expenditures for repair or removal. These cases include three industrial plants, one thermal pow plant and 10 municipal water treatment systems. The consequences of biofouling at these plants range fr m reduced water flows and pressures, abandonment of intake pipes, temporary shutdowns and the install tion of chlorination facilities to kill the organism prior to removal. Each of these cases are summarized in T able 1. The locations of these occurrences are also shown in Table 1.

Left unattende d, mussel infestations can disable fire protection systems in power plants and industrial facilities. Of p rticular concern to power utilities is the lodging of mussels in small diameter pipes leading to over-heating of cooling condensers and major damage to the generating facility. Reduced flows in an industrial plant can res ult in reduced production, higher unit production costs and reduced profitability.

Shutdowns of an industrial plant such as a refinery can involve expenses of more than $750,000, not counting lost production a nd revenues (Atwell, 1990). So far, Ontario establishments have been spared such extreme consequences.

Municipal water treatment plants that experience reduced flows because of mussel blockages suffer increased operating costs (ie. increased $ per unit of water pumped) and reduced energy productivity. A municipal water treatment plant at Monroe, Michigan, one of the first establishments in all of the Great Lakes to experience zebra mus el infestations, had to install a temporary intake system while mussel encrusted components were cleaned or replaced. The city of Monroe spent over $6.3 million on cleaning, repairs and the temporary pumping fa cilities (Lepage et.al., November 1989). The water intake structures and pipes at West Lorne and Tilbury, Ontario had to be abandoned because of infestations and new installations are under construction at a cost of a bout $5-6 million for the two projects.

To date, capital and other one-time expenditures directly attributable to zebra mussel biofouling in Ontario amount to about $8.7 million as shown in Table 1. Compared with the relevant budgets and expenditures normally as sociated with Ontario Hydro, industrial plants and municipal water and sewage utilities, these expenses ar e as yet relatively modest. However, they may be a portent much greater financial requirements in the future.

Once in place, re moval of colonies from intake structures and pipes is a daunting and arduous task. Moreover, experience and technologies available in North America are as yet limited. A variety of methods and technologies are bein g investigated either to remove zebra mussels already ensconced in a water intake system or to prevent their establishment in the first place.

Methods for the removal of Dreissena polymorpha colonies currently in use include hand scraping by divers, "hydro blasting" w ith high pressure hoses, pulling mechanical scraping devices called "pigs" through an intake pipeline, killing mussels prior to removal with hot water or chemicals such as chlorine and abandonment and replace ment of clogged pipes. Factors that impede these efforts and raise the costs of their implementation include w eak pipes that cannot withstand the stresses of mussel removal, limited access to pipes by divers and clean ing equipment, the need to shut down plants to effect removal and repairs and the ability of the adult musse l to withstand extreme temperatures and biocides such as chlorine if the procedures are not applied properly. Hand scraping, pipeline cleaning contractors and chlorination were employed at the three industrial plants not d in Table 1.

In Europe where Dreissena has been endemic for many decades, intake structures and pipes have been "twinned" to permi uninterrupted operation while one pipe is being cleaned. Intake pipes are also designed to facilitate clea ing and mussel removal.

Other, somewhat esoteric, mussel removal methods of unknown efficacy have been reported recently including electric shock a d acoustic (sound) devices to shatter the animal (Davidson, August 9, 1990).

A variety of chem ical biocides in addition to chlorine are being tried out to help remove infestations and prevent their formati on. Potassium permanganate, oleanolic acid glucoside (an active ingredient in the African soapberry), brom ine, copper sulphate, cyanuric acid, ammonium nitrate and ozone are all under investigation. So far, chl orine has proven to be the most cost-effective material available.

For the hundreds of Great Lakes water-using establishments not yet encrusted with zebra mussels,

TABLE 1 CURRENT INFESTATION OF ZEBRA MUSSELS IN ONTARIO AND THEIR EFFECTS

PLANT/LOCATION	INFESTATION EFFECTS	RESPONSES	POTENTIAL EXPENDITURES	SOURCE
Ford Engine Plant, Windsor, Detroit River.	- Mussels found in cooling and service systems and intake pipe. - Clogging and reduced flows in pipes < 4".	Temporary chlorination.	About $3,000 for one week.	Personal interview, Aug. 31, '90
General Motors, Parts Plant, St. Catharines, Lake Ontario.	- Mussels in fire reservoir, intake strainer, service system.	Chlorination, 2 weeks. Follow-up 1990.	May - $130,000 for 2 weeks. Sept. - 205,000 for 2 weeks.	Paul Smith, GM, Personal communication, Aug. 1990.
H. J. Heinz, food processing plant, Leamington, Lake Erie.	- Intake pipe clogged.	Mechanical cleaning and scraping.	Not available	Canada Pipeline Cleaning Ltd. Personal comm.
Ontario Hydro, Nanticoke Thermal Generating Station, Lake Erie.	Mild infestation of service water system, one clogged.	Some mechanical scraping and removal; chlorination system extended.	Extension of chlorination system - $300,000; Biobullet $8,000; Technicians at Nanticoke - $38,400/yr. Cleaning part of annual maintenance. Corporate solution $672,000 per year.	Ontario Hydro
Tilbury Water Treatment Plant, Lake Erie	Mussels in intake pipe; reduced flow capacity by 45%.	Replacement of intake pipe; extension of chlorination.	$2,126,000	Ministry of the Environment.
West Lorne Water Treatment Plant	Mussels in intake pipe; reduced flow capacity.	Extension of chlorination system; replacement of intake pipe and low lift system.	$4,300,000	Ministry of the Environment
Amherstburg Water Treatment Plant	Reduced flow capacity.	Extension of chlorination.	$45,000	Lafontaine et al. (1990)
Blenheim Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	$100,000	Lafontaine et al. (1990)
Kent County Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	$65,000	Lafontaine et al. (1990)
Harrow-Colchester Water Plant	Reduced flow capacity.	Extension of chlorination system.	$45,000	Lafontaine et al. (1990).
Elgin Water Trmt. Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	$137,000	Lafontaine et al. (1990).
Belle River Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	$130,000	Lafontaine et al. (1990).
Tecumseh Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	$45,000	Lafontaine et al. (1990).
Mitchell's Bay Plant	Reduced flow capacity.	Extension of chlorination system.	$30,000	Lafontaine et al. (1990).

methods of prevention are of particular interest. Placement of intake pipes in deeper water, burying intake pipes and structures where feasible, specially designed intake structures with screening and devices to continuously clean screens, maintenance of water flows above 2.5 metres per second, anti-fouling coatings on exposed surfaces and treatment with chlorine, ozone or other approved biocides periodically to kill larvae and juvenile animals in the system are all under trial and investigation.

Where facility configurations permit, periodic flushing with hot water (above 40 C) has been found to be effective. This approach is currently employed at a small thermal electric power plant operated by the Welland Canal Authority (Aquatic Sciences, 1990). So far, the major water-using installations in Ontario, such as Ontario Hydro and municipal water treatment plants, are installing systems to chlorinate their intake water during 6 months of the year to kill veliger larvae that get into the systems. Such facilities consist of a tube or pipe to carry the chlorine to the lake end of the intake pipe as well as chlorination pumps, meters and storage tanks.

Although chlorine is widely used as an oxidizing agent in industry and a disinfectant for sewage treatment and water treatment plants, its use in zebra mussel control defines it as a pesticide and requires that a license from the Ministry of the Environment be obtained for this application.

An integral part of a program of prevention is monitoring using "bio-boxes" to determine the presence of veligers and the effectiveness of controls and inspections by divers and remote TV cameras. In addition, research on a variety of removal and preventative measures are being carried out primarily by government and some larger industrial firms such as Ontario Hydro.

Another form of "control" involves identifying and encouraging natural predators of Dreissena in North America. This approach would help control the beds of mussels that contribute to beach infestations and accumulations. Certain species of diving ducks consume zebra mussels and appear to be increasing their populations around infested localities. One specie of indigenous North American fish, the American drum, also eats zebra mussels but is itself of little interest to recreational and commercial anglers.

Finally, relevant government authorities are reviewing legislation and regulatory requirements for the treatment and disposal of ballast water from foreign ships. While it is too late for the zebra mussel, tighter controls could prevent the unintended immigration of new undesirable species.

6. POTENTIAL COSTS OF RESPONSES TO BIOFOULING

If the Dreissena invasion continues unchecked, many more direct water-using facilities will be at risk from biofouling. In order to avoid the potentially serious damages that are possible, these establishments must choose whether to install preventative measures or to implement a periodic cleaning and removal program that is frequent enough to ensure that druses do not become established. Systematic monitoring involving at least two visual inspections by divers each year and the installation of devices such as "bio-boxes" to detect veligers would help to determine when removal or chemical control measures must be applied.

Preliminary estimates of the costs of a monitoring program and of installing or modifying chlorination systems at 8 Ontario Hydro power plants, 86 municipal water treatment plants and 67 industrial plants that are located on the Great Lakes and are at risk from zebra mussel infestations have been developed. The estimates, which are summarized in Table 2, are disaggregated by three geographical areas:

Area A Currently infested shoreline between Windsor and Niagara-on-the-Lake.

Area B Shorelines at Risk from Kincardine to Windsor and Niagara-on-the-Lake to Cornwall.

Area C Rest of the Great Lakes.

Other types of control systems may be applied in these plants, such as ozonation, but alternative systems are likely to be much more costly and, as noted, chlorination is currently the system of choice among those agencies most directly involved.

Ontario Hydro thermal and nuclear generating stations already have chlorination systems in place and the capital cost estimates involve modifying the chlorination systems to introduce the chlorine at the intake structure out in the lake. An amount of extra chlorine will likely be required after these modifications are made but could not be estimated at this time. Since few if any of the industrial plants have chlorination systems in place, all of the chlorine used will be incremental. The costs of chlorine shown in Table 2 that may be used by industrial plants are based on a dosage of 5 ppm.

Costs of cleaning and removal could be estimated only for Ontario Hydro facilities, based on reported zebra mussel removal costs incurred at the Detroit Edison thermal power plant at Monroe, Michigan (Kovalak et al. 1990). Estimates for intake pipe cleaning and removal at municipal water treatment plants and industrial facilities could not be generated at this time.

Estimates of potential expenditures for monitoring activities are presented for each of the three types of water-using plants as well.

Estimation procedures, algorithms and the input information used to prepare the figures shown in Table 2 are detailed in Donnan and MacKay (forthcoming).

It is clear from Table 2 that municipalities will likely have to incur the majority of these potential retrofitting expenditures or about $148 million out of $165 million in total expenses for all "Zones." These estimates are also over and above the expenses listed in Table 1.

If the systems installed for prevention are successful, little if any removal and cleaning costs will have to be incurred at municipal and industrial plants. Expenditures for chlorine and monitoring may be underestimated because increased demand for chlorine chemicals and monitoring services (ie diving) could push up prices over the next several years. Estimates of monitoring for each sector are probably underestimated in any event.

Not included in these estimates are $3.5 million in research projects committed by Ontario Hydro over the next 3 years and an unknown amount to be spent on zebra mussel research by the provincial government during the foreseeable future (Spencer, February 1990).

One-time expenses of $165 million and annual expenditures of about $10 or $11 million per year, while not inconsequential, are not large in comparison to other expenditure categories incurred by the affected establishments. On the other hand, there are many uncertainties associated with these estimates which could result in upward revisions.

It does not appear that the zebra mussel will impose intolerable financial burdens on Great Lakes water users during the near future. Moreover, the estimates presented here represent opportunities to the firms and agencies which offer goods and services in response to zebra mussel incursions.

A very tentative conclusion is that the consequences of the zebra mussel infestations and the costs incurred to respond to them will not cause undue economic or social repercussions so long as Great Lakes water users are vigilant and implement control or preventive measures in time. One of the best investments that can be made at this time would be increased monitoring and surveillance by all parties at risk.

7. IMPLICATIONS FOR RECREATIONAL BEACHES

At least 10 Lake Erie beaches in the southwest part of Ontario have experienced nuisance levels of littering by zebra mussel shells. Using a Beach-Use model developed by Usher, Ellis and Michalski (1987), the implications of reduced aesthetics and attractiveness of beaches in terms of reduced visitation and use rates has been explored.

The model includes an "attractiveness index" which may be used to classify a particular beach as "excellent", "very good", "acceptable", "marginal" and "unsatisfactory". Ten Lake Erie beaches in Essex, Kent and Elgin Counties that are included in the model have recorded accumulations of zebra mussel shells. The "attractiveness index" for these beaches were reset to "marginal" and "unsatisfactory" and the resulting shifts in beach attendance or visitation were estimated with the model.

If the zebra mussel becomes more widespread, it may affect beaches over a much wider range of the Great Lakes. In this analysis, it was postulated that all beaches could be adversely affected by Dreissena from Kincardine (on Lake Huron) to Cornwall, Ontario, on the St. Lawrence River at the Ontario-Quebec border. The "attractiveness index" was reset to "marginal" and "unsatisfactory" for these beaches and the model run for each scenario.

The results of these analyses are shown in Table 3. In the 10 beaches currently infested with zebra mussels, beach use occasions could be reduced by as much as 18% if the effects caused by zebra mussels only partially reduced the attractiveness of the locations. However, if the adverse effects are perceived by people to be of major importance, beach attendance would be reduced by as much as 50%.

The model assumes that people would go to other beaches in Southwestern Ontario which are located on inland waters or on Lake Huron and the Georgian Bay. Expenditures associated with these beach occasions (ie travel, food, accommodation, etc.) would not likely leave the province under either level of perceived attractiveness because the total number of beach use occasions in Ontario are assumed to stay constant.

Real losses in utility and enjoyment may be experienced by beach users who continue to visit mussel infested locations or those who go to other locations which then become more congested.

Where it is assumed that all beaches between Kincardine on Lake Huron and Cornwall on the St. Lawrence River experience reduced attractiveness (to "marginal"), the number of visits to these beaches falls by about 12.5%. Under these conditions, people would likely shift their visitation north to the Georgian Bay, to inland lakes in Eastern Ontario, the Southwest and around the "Golden Horseshoe".

There are, as yet, no clear means of preventing the spread of Dreissena along shorelines and Further deterioration of beach quality by mussel shells could have severe local economic effects but research is needed to monitor and enumerate these consequences.

8. OTHER BIOLOGICAL INVASIONS OF THE GREAT LAKES

At least 38 species of fish have been introduced into the Great Lakes since 1819, either deliberately or intentionally (Emery, 1985). Ten of these "exotic" species are recognized has having major influences on aquatic ecosystems in the Great Lakes and their uses by people. Four of these earlier "invaders", the sea lamprey (*Petromyzon marinus*), the alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*) and the white perch (*Morone americana*) have had particularly adverse effects.

Lamprey eels were present in Lake Ontario since the early 1980's but only gained access to the upper Lakes through the Welland Canal in 1921 (Christie, 1974). However, unlike the zebra mussel, it took another 20 years for this invader to encroach upon the affairs of man. The other exotic species were introduced before or just after the turn of the century. Major effects and consequences were not realized until the 1940's and 1950's.

The consequences of concern were the decline of important indigenous species in the Great Lakes, including the lake herring (*Coregonus artedii*), certain varieties of walleye and the lake trout (*Salvelinus namycush*), as a result of predation, competition and external habitat destruction.

The predatory activities of the sea lamprey have been particularly damaging to the highly valued lake trout (*Salvelinus namaycush*), whitefish (*Coregonus sp.*) and burbot (*Lota lota*) populations native to the open waters of the Great Lakes. By 1949, Lake trout populations and commercial catches in Lakes Huron and Ontario collapsed and by the early '60s, the lake trout fishery in Lake Superior was wiped out (Christie, 1974). Similarly, lake whitefish (*Coregonus clupeaformis*) suffered lamprey predation when trout and burbot were no longer available. Commercial catches of whitefish were virtually eliminated in Lakes Michigan and Huron by 1954 and drastically reduced in Lakes Superior and Ontario by the early 1959's due in great part to lamprey predation (Christie, 1974).

TABLE 2: SUMMARY OF COST ESTIMATES FOR THE CONTROL OF ZEBRA MUSSELS IN ONTARIO
(MILLIONS OF $)

ONTARIO HYDRO
POWER PLANTS: 8 PLANTS

	PREVENTION CAPITAL	O&M/CHLORINE	REMOVAL & CLEANING	MONITORING	
ZONE A (1)	0.50		0.38		
ZONE B (2)	0.90		0.62		
ZONE C (3)	0.40		0.25		
TOTAL:	1.80	N/A	1.25	0.72	

MUNICIPAL FACILITIES: 86 PLANTS

	PREVENTION CAPITAL	O&M/CHLORINE	REMOVAL & CLEANING	MONITORING	
ZONE A	30.30				
ZONE B	92.90				
ZONE C	25.30				
TOTAL:	148.50	N/A	N/A	0.86	(4)

INDUSTRIAL PLANTS: 67 PLANTS

	PREVENTION CAPITAL	O&M/CHLORINE	REMOVAL & CLEANING	MONITORING	
ZONE A	5.00	5.20			
ZONE B	8.30	2.30			
ZONE C	1.10	0.00			
TOTALS:	14.40	7.50	N/A	0.67	(4)

TOTALS:

ZONE A -	35.80	5.20	0.38	
ZONE B -	102.10	2.30	0.62	
ZONE C -	26.80	0.00	0.25	
	-----	-----	-----	-----
GRAND TOTAL:	164.7	7.50	1.25	2.25

NOTES:

(1)ZONE A: CURRENT INFESTED ZONE - WINDSOR TO NIAGARA
(2)ZONE B: SHORELINES AT RISK - KINCARDINE TO WINDSOR
AND NIAGARA-ON-THE-LAKE TO CORNWALL
(3)ZONE C: REST OF GREAT LAKES
(4)MONITORING FOR MUNICIPAL AND INDUSTRIAL FACILITIES CONSISTS OF DIVES TOTALLING $5,000 FOR 2 DIVES PER YEAR, AND $5,000 FOR OPERATING AND CAPITAL COSTS OF BIO-BOXES

TABLE 3: POTENTIAL CHANGES IN DAILY VISITS TO BEACHES RESULTING FROM REDUCED ATTRACTIVENESS (000's of occasions)

	ATTRACTIVENESS INDEX RATING					
	MARGINAL			UNSATISFACTORY		
	ORIGINAL USE	NEW USE	% CHANGE	ORIGINAL USE	NEW USE	% CHANGE
10 BEACHES CURRENTLY INFESTED WITH DREISSENA	1,542	1,266	-17.90%	1,542	822	-46.69%
ALL BEACHES BETWEEN KINCARDINE AND CORNWALL	10,013	8,718	-12.93%	N/A	N/A	N/A

After the collapses of populations of predatory fish species, smelt stocks increased rapidly in Lakes Ontario and Superior, alewife populations burgeoned in Lakes Superior, Huron and Michigan, cisco (*Coregonus johannae*) stocks expanded, at least briefly, in all the Lakes and the indigenous lake herring (*Coregonus artedii*) stocks collapsed throughout the region. Researchers believe that lamprey predation together with overfishing are the primary causes of these major aquatic population disturbances (Christie, 1974).

The measured effects of these exotic species have all occurred during the past 40 years and the population dynamics of aquatic populations in the Lakes have yet to be stabilized. The primary linkages to man in each case are reductions in commercial catches of indigenous species. Substantial recreational utility has undoubtably been lost as a result of population collapses of various highly prized game fish. However, monetary values associated with efforts to control the invader and with the profit and enjoyment (utility) of restoring desired fish species that result of this control has been enumerated only for the lamprey eel.

In 1955, the Great Lakes Fishery Commission (GLFC) was formed by treaty between the U.S. and Canada to promote and coordinate efforts to control the sea lamprey and restore lake trout populations in the Great Lakes. Commission sponsored research eventually lead to the development of 3-trifluormethyl-4-nitrophenol (TFM), a selective toxicant which has been used since the early 1960's to kill the ammocoetes larvae of the lamprey in nursery streams (Applegate et al., 1961).

These control efforts have lead to a partial recovery of lake trout and whitefish populations in many areas of the Great Lakes. Lamprey control, together with salmonid stocking programs in the Great Lakes are the primary fisheries management activities carried out by federal, State and provincial (Ontario) governments on the Great Lakes. Sport and commercial fishing interests are the primary beneficiaries of these programs. Sport fishing for introduced salmonids, lake trout, walleyes, whitefish and other species has come to dominate commercial fishing on the Great Lakes in terms of direct expenditure, associated employment and political attention. (Talhelm, 1987; Spaulding and McPhee, Nov. 28, 1989).

Since its inception in 1955, the Great Lakes Fishery Commission has spent several millions of dollars each year on sea lamprey control. In 1988, the Commission spent $6.2 million (Canadian) on the sea lamprey control program, $1.2 million on research and barrier dams and $ 0.6 million on administration or about $8 million in total (Spaulding and McPhee, Nov. 1989). The funds originate from the U.S. and Canadian governments.

As part of an evaluation of the Commission, Spaulding and McPhee (Nov. 1989) estimated the monetary values associated with recreational fishing that would be reduced if the sea lamprey control program were to be terminated in the Great Lakes. Increased lamprey predation on salmonids would substantially reduce the fish available for harvesting by recreational fishermen. Salmonid fishing days would be lost as the result of three behaviourial responses: 1) some anglers that fish for salmonids will no longer fish in the Great Lakes; 2) some salmonid anglers will switch to non-salmonid species, and 3) increased angling effort on non-salmonids will cause some non-salmonid anglers to abandon the Great Lakes as well.

The total net value of these consequences was estimated at $318 million (Canadian) per year (Spaulding and McPhee, Nov. 1989). Because salmonid fish only account for about 3% of the 1988 Canadian landed value, lamprey control would have little effect on that sector. The authors note that these consequences should also be attributed in part to salmonid stocking programs which cost a total of $10.2 million (Canadian) in 1988 (Spaulding and McPhee, Nov. 1989).

Therefore, while sea lamprey control costs about $8 million (Canadian) each year, the recreational utility that could be lost if the control measures were eliminated would amount to over $300 million per year. This latter value would be comparable to the values associated with the damages that Dreissena could cause if no defensive expenditures or control measures were incurred.

9. CONCLUSIONS

To date, capital and other one-time expenditures directly attributable to 14 documented zebra mussel biofouling cases in Ontario amount to about $8.7 million.

Ontario municipalities around the Great Lakes will likely have to incur the majority of potential expenditures for zebra mussel prevention and control or about $148 million out of total $165 million. Compared with the relevant budgets and expenditures normally associated with Ontario Hydro, industrial plants and municipal water and sewage utilities, the expenses that have been incurred to date and that have been forecast are as yet relatively modest. However, they may well be a portent much greater financial requirements in the future.

A very tentative conclusion is that the consequences of the zebra mussel infestations and the costs incurred to respond to them will not cause undue economic or social repercussions so long as Great Lakes water users are vigilant and implement control or preventive measures in time. One of the best investments that can be made at this time would be increased monitoring and surveillance by all parties at risk.

There are, as yet, no clear means of preventing the spread of *Dreissena* along shorelines and beaches. Further deterioration of beach quality by mussel shells could have severe local economic effects but research is needed to monitor and enumerate these consequences.

The zebra mussel is the most recent of many biological invasions of the Great Lakes over the past century. Hopefully, it will be the last.

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ECONOMICS AND TECHNICAL CHANGE: THE WATER RESOURCE CONUNDRUM.

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ABSTRACT

One of the most potent, but least understood, functions of a market system of economic organization is its ability to motivate technological change. The market system provides incentives for private gain, which, in turn, leads to the generation of new technologies. The key to this process lies in the ability of prices to reflect accurately the value of the resources devoted to respective economic activities.

A major problem of environmental management arises because environmental resources are, almost without exception, undervalued in relation to their contribution to economic activities. This paper uses the case of municipal and industrial water pricing to document the almost-negligible cost of water resources in relation to the costs of other goods and services, and to production costs. The data are based upon recent surveys of municipal and industrial water prices. These survey indicate municipal water prices in Ontario (including sewer charges) averaging less than $0.60 per cubic meter, and industrial charges which are substantially below 1% of production costs.

The paper concludes by discussing the implications of the current state of water pricing for technological change in the water industry, and with suggestions for improvement. The overall thesis is that until water prices reflect better the value of the resource to society, incentives for technological change will continue to be significant retarded.

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[1] The opinions expressed in the paper are those of the authors, and not necessarily those of Environment Canada

1. INTRODUCTION

Since the 1960s, interest in the environment and its problems have grown at an ever-increasing rate. To-day, environmental issues, ranging from pollution to export, are usually listed among the top three issues in public opinion polls. We do not have to think very long to find the reasons for this "popularity".

Water pollution problems raise concerns in many parts in many areas of the country, notably the Great Lakes and major estuarine areas. Although water management has taken significant strides in overcoming certain pollution problems, significant ones remain, such as toxic substances. Water shortages are common in many areas, most importantly in the Western Interior, but even in southern Ontario, a peninsula built into the heart of the world's largest freshwater body. Canadians have slowly realized that 9% of the world's annual renewable water supply is not, by itself, a guarantee of freedom from water shortage. Resource distribution and pollution have fixed that perception. Capital shortages for water projects are so severe that the infrastructure of major urban areas is deteriorating rapidity.

Each of these problems has technological dimensions. Some are obvious, such as the need to upgrade and improve conveyance and treatment methods. Others are not, and this paper addresses one of those - namely, the mechanisms which underlie technological developments, and which allow the advancement of living standards in many societies throughout the world, but which seem to have been blunted in their effects on the use of environmental resources such as water. It is clear that technical developments do not just "happen", or fall from the sky. On the contrary, there are very clear reasons why change occurs, and, indeed, why it occurs in some areas and not in others. In water management, the mechanisms underlying technological change are not well understood, and have rarely even been acknowledged. We believe, however, that they lie at the heart of any hopes for significant improvements in environmental management.

2. ECONOMICS AND TECHNICAL CHANGE

Schmookler (1966) defined technology as "the social pool of industrial arts." Clearly, technological change is an change in this pool. The central issue is what causes these changes, in other words what conditions have to be present for advancement to occur. This question has concerned many generations of economists and social scientists, and it is to a brief explanation of their findings that we now want to turn.

The concern of people over resource scarcity reaches back in history at least into the eighteenth century. Well before Thomas Malthus explained how unrestrained population growth would be held in check and in misery by the limited amount of food producing land, the Phisiocrats of eighteenth century France and the great Adam Smith reasoned that all wealth ultimately came from the land and so the limits of land would limit production. This concern over physical limits to productivity has proven less than accurate for many areas of the world, at least into the latter part of the twentieth century. As Charles Schultze stated:

> "Living standards in modern Western countries are, by an order of magnitude, superior to those of the early 17th century. Had the triumph of the market meant only a more efficient use of technology and resources then available, the gains in living standards would have been minuscule by comparison. What made the difference was the stimulation and harnessing of new technologies and resources."

This statement supports strongly the findings of Nobel prize winner Robert Solow, who demonstrated that over 85% of technological advancement in the U.S. economy during a forty year period was due to the operation of economic forces through the medium of the marketplace (Solow, 1955).

The conclusion of importance here is that economic forces are largely responsible for incentives which lead to technological change[1]. On the supply side, the progression of technology has vastly increased the resources available, through discovery of new reserves and stocks of everything from petroleum to fish. Supplies have been expanded even more by advances enabling the use of less accessible resources, of lower quality, and lesser concentrations. Even land, though limited in the spatial sense, has been augmented enormously in its capacity to produce crops (Pearse and Tate, 1990).

On the demand side, technology has progressively reduced and eliminated our dependence on particular resources for particular resources for particular purposes, broadening the range of materials available to producers, and improving the suitability among them. Timber is no longer needed to construct buildings and ships because there are now a dozen new materials to choose from. Societies no longer need copper to transmit energy and messages because materials like aluminum and fibre optics, made of much more ubiquitous raw material, will do the same job. Indeed, we no longer need any materials for these purposes, because electronic signals can be transmitted without them. All this innovation has more than offset the depletion of resources through consumption. Notwithstanding the enormous economic growth of the past century, the demand for almost all natural resource commodities and food has risen slower than the supply. The result is that the real price of natural resource products -- that is, the cost relative to manufactured goods, or to all goods and services taken together -- has gradually declined (Pearse and Tate, 1990).

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[1] Military need constitutes one of the other primary technological change stimulants, but this need has proven of less importance than economic incentive.

These findings, which are readily acknowledged by most resource specialists, lead to a cruel paradox environmentally. On the one hand, technology has led to the creation, in Western societies, of enormous gains in living standards for all groups in society, although, undoubtedly, not all have benefited equally. On the other, the same technology and productivity has caused substantial, and in some cases catastrophic, environmental degradation. Thus, why, for example, should economists advocate the use of economic instruments to help solve environmental problems when economic forces have done so much harm?

If various sectors of the economy are examined carefully with respect to their uses of environmental resources, we quickly find that economic forces, such as the interplay of supply and demand to determine realistic prices, have been almost totally absent. Thus, it is no surprise that technologies are extremely traditional, resources are overused, wasted and, in some cases, destroyed. It is almost as if society has ignored one of its strongest forces, namely economic incentive, and then attempted to do an effective job of coping with environmental management (Tate, 1984). The sooner that economic forces are recognized as being of central importance in promoting technological change in the water industry, the quicker and more effectively will water managers be able to do their jobs.

3. TECHNOLOGY AND WATER RESOURCES

What is meant by traditional technology? Certainly, the water resource trade journals, on the surface, seem to suggest that water technologies have developed substantially. The Science Council of Canada even suggests that an export industry should be built of Canadian technology.

Examples of the persistence of traditional technologies are easy to identify. The following examples are illustrative, although by no means exhaustive. First, Environment Canada's industrial water use surveys have demonstrated that the percentage of industrial water deriving from recirculation has fallen over the 1972-1986 period (Table 1). The concept of a use rate is a simple way of looking at this. If gross water use, or the total amount of water used in producing a product is divided by total water intake, and multiplied by 100%, the result is a use rate. The higher the rate, the higher the level of recirculation. In almost all cases, the use rate fell, showing that recirculation rates declined during this 14-year time span.

Second, the average Canadian per capita water use from municipal systems is 350 litres per day, second only to that of the U.S., and over double that of many European countries. Also, of the water pumped in many Canadian municipalities, less that 75% can be accounted for by deliveries to customers. Third, water use inside the home is excessive. The typical toilet uses 20 litres per flush, and showers use over double the amount of water required for effectiveness. Postel (1985) showed that a typical North American home could save over $100 per year in energy costs alone by using water efficient showerheads. Fourth, recent research done at McMaster University (Patry and Takacs, 1990) showed that waste treatment plants are less efficient the greater the amount of water pumped through them. Fifth, irrigation in Western Canada supports the growth of crops that could probably be grown more cheaply in more humid areas. Irrigation causes enormous amounts of water consumption in an area where there exist much more highly valued water uses. Finally, in all parts of Canada, we afford industries free access to waterways for waste deposition. Serious water pollution problems have resulted.

Table 1 Use rate (%) for Canada and Ontario, 1972 - 1986

Year	Canada		Ontario	
	Total	Manufacturing	Total	Manufacturing
1972	172	233	148	208
1981	152	208	120	185
1986	142	198	114	188

Note: The "total" industry columns include mineral extraction, manufacturing and thermal power generation sectors. The use rate equals (total gross use/total intake) x 100%.

Improvements are certainly possible. Research in water use by industry (Kollar and MacAuley, 1980) showed that water can be recycled up to nine times through advanced industrial plants. In terms of the use rate measures of Table 1, this would give rates upwards of 900%. Jank (1987) has found that the capacity of a waste treatment plant can be effectively doubled through the use of computerized controls of plant processes. The energy savings possible through the use of water efficient fixtures has already been mentioned. Research at Environment Canada has shown that petroleum-like material can be recovered from waste treatment plant sludge. Changing industrial systems with water handling as a design criterion is effective in both saving water and lowering costs (Ayers and Kneese, 1968). These are but a few of many examples of technological change possible in the water industry.

4. THE ROOT OF THE CONUNDRUM: WATER VALUATION

It was suggested earlier that economic forces have not been at work in the water resources field. This almost complete failure to use market forces in helping to allocate water resources lies at the root of the retardation of technological in the water industry. This section presents two examples which illustrate this lack of attention to economic factors.

(Before going any further, one point is important in qualifying the argument presented here. The operation of an unfettered market is not always superior, and, in the environmental case, some mix of regulation and incentive is probably the best approach. However, the power of market forces offers great advantages, which have to be recognized by the water management profession.)

Environment Canada has conducted a number of surveys of retail prices to the users of municipal water services across Canada. These surveys were undertaken to establish some baseline information on the conditions faced by water consumers. In other words, what are the "signals" being received by consumers about the value of water services?[2] The results of these surveys have interesting economic implications for the problem posed in this paper.

The surveys show that about one-third of the price structures in use by Canadian municipalities comprise what are commonly referred to as flat rates. The cost of an extra, or marginal, unit of water under this type of structure is zero. In other water becomes a free good, and used accordingly in a wasteful manner, regardless of the need to conserve.

Most of the other structures in use are termed declining block rates, under which the price of water declines progressively with increasing use. The rationale for this type of structure, clearly stated by the A.W.W.A. (1983), has been discredited in much of the professional literature (Hirschleiffer et al., 1960; McNeill, 1987). The remaining structures are constant unit charges (i.e. a constant price per unit of use, regardless of quantities used), increasing block rates or some other more complex types of arrangements

Thus, a first major observation is that price structures actually encourage overuse of public water supplies. This has been witnessed by the elevated costs of supplying water and waste treatment services, and the consequent overbuilding of water facilities. The current financial problems in the municipal water industry (FCM, 1985) are hardly surprising under these conditions. Worse still is the almost complete absence of incentives for technological change in the industry today.

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[2] Note that these surveys made no attempt to link consumer prices to the costs of providing the service. Thus, definitive judgements about whether water prices are effective in terms of cost recovery cannot be made from the data collected.

This situation is compounded when the unit prices for water (where these are relevant) and total retail prices are examined (Table 2). Three observations are relevant here. First, unit, average and total prices are very low in comparison with the prices of other goods and services. For example, the cost if a cubic meter of soft drink, the next cheapest common liquid in use is about $500.00. Second, the price of water includes delivery to the home and waste removal. Third, prices have increased over the three-year period covered by the table, but are still relatively insignificant in relation to the costs of other services, such as electricity. The "signal" being passed to consumers, accordingly, is that the service is cheap to produce, and that waste is an insignificant problem.

The second example is drawn from the 1981 and 1986 industrial water use surveys, conducted nationally, covering about 7,000 industrial establishments (Tate and Scharf, 1985, 1989). Water costs to industry totalled $421 million in 1981 and $585 million in 1986 (current dollar terms). In both cases, these amounts were under 1% of total production costs. In irrigated agriculture, water costs are subsidized 85%-90% by public agencies, which construct the infrastructure, charging irrigators low flat charges per hectare for the actual commodity. In these cases, again, water prices are insufficiently low to provide incentives for rational water use and for technological change.

5. INTERPRETATION AND CONCLUDING REMARKS

The data provided in this paper show that Canadian water prices are very low. The implication for water use in a static situation is one of overuse, both in a quantitative sense, and in the sense of cheap or free use of water courses for waste removal. Dynamically, low prices mean that little or no account is taken of economic factors in forecasting water demands, resulting in forecasts which are biased upward and resultant overbuilding of systems.

Low prices also mean that cost recovery is not achieved. One implication here is that capital shortages frequently occur and that other public infrastructure often take precedence over water infrastructure. The municipal infrastructure financing problem identified by FCM (1985) is therefore not surprising.

Of most relevance for this paper is that current economic practices provide no incentive for capital-driven technological change. For instance, the industry is unable to attract the voluntary research funds, which are critical for technological change. The industry is critically in need of technological upgrading, similar to that which has occurred in connection with the energy industry, an equally important infrastructural element. However, in contrast to that industry, there are few economic incentives in water. We can confidently predict that few of the needed changes will occur until economic practices are radically reformed.

Table 2 Selected municipal water price indicators, Canada, 1986 and 1989

Indicator	1986		1989	
	Canada	Ontario	Canada	Ontario
a. Unit prices (cents/m^3)				
1. CUC	38	40	52	65
2. BR-first	48	43	62	57
3. BR-last	29	24	39	41
b. Retail prices ($/month)				
1. 10 m^3/month	10.90	11.49	14.40	15.96
2. 25 m^3/month	14.77	15.10	18.15	21.00
3. 35 m^3/month	16.08	17.39	20.88	24.57
c. Average prices (cents/m^3)				
1. 10 m^3/month	109	115	144	160
2. 25 m^3/month	59	60	73	84
3. 35 m^3/month	46	50	60	70

Notes: CUC = constant unit charge.
BR-first = price per m^3 in the first block.
BR-last = price per m^3 in the last block.

NOTE: All prices include the relevant sewer surcharges.

Sources: Tate (1989); Tate and Lacelle (1990)

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MODELLING MUNICIPAL WATER SYSTEMS FOR DEMAND MANAGEMENT

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INTRODUCTION

Water demand management is something not extensively practised by Ontario municipalities (Kreutzwiser & Feagan, 1988), therefore it is best placed in the context of the prevailing water management philosophy. Traditionally most demands for water have been viewed as legitimate so that municipalities generally feel that they must provide water for all users and for all purposes. This is the philosophy of supply management and it is reinforced by the perception that this province has an abundance of water. Although this may appear true, the annual runoff into the Great Lakes is only 1% of their volume; also, local population densities and degradation of water quality can and do lead to short and/or long term shortages of water. In addition, it is usually assumed that water provision is relatively inexpensive. Even if this were the case, the implied costs of providing wastewater treatment are rarely considered in a decision to expand water supply, yet few would consider those costs unimportant. Supply management practised alone can lead to overinvestment in structural solutions (pipelines, sewage treatment plants, etc.) to water problems. Demand management seeks to modify the amount of water demanded rather than the amount of water supplied. It is becoming increasingly attractive for economic and availability reasons and also because the issue of water resource allocation is involved. Water not used by municipalities is water available for other uses, particularly in-stream or in-situ uses, e.g. for maintaining aquifer levels for the benefit of the agricultural community.

The Regional Municipality of Waterloo is currently facing short term water shortages in the Tri-City area (Kitchener, Waterloo and Cambridge) due to growth of population and industry. The supply augmentation project under construction will provide water at many times the cost of water from current sources. Also, part of the water supply of Kitchener-Waterloo currently comes from aquifers situated in the surrounding rural municipalities, who are concerned that water withdrawals by the cities are lowering water table, to the detriment of the farming community. Also, the contamination of the Elmira water supply by DMNA is putting further stress on the Tri-City area water supply, since a pipeline is being built from Waterloo to Elmira for the purpose of supplying Elmira's needs.

This study is developing a model of the water system which can be used by a municipality to examine the potential for and the cost effectiveness of demand management. Such a model should integrate the supply and distribution of water, usage of water and the collection and treatment of wastewater (Robinson & alia, 1984).

GENERAL SYSTEMS MODELLING SOFTWARE: STELLA

Modelling was done with STELLA (Richmond & alia, 1987), a general systems modelling application for Macintosh microcomputers. Macintoshes computers can now read and write to IBM formatted diskettes, so that input from and output to the IBM environment is now practical. In STELLA, model variables are represented by graphical elements. These elements are laid out on the computer screen as in a computer drawing application. An example of a simple model is shown in Figure 1. In this example, the variable "serviced_population" is derived from integrating "population_growth" over time, and is therefore represented by a rectangular element, called a stock. The circular elements, representing constants, algebraic formulas or graphical functions, are called converters.

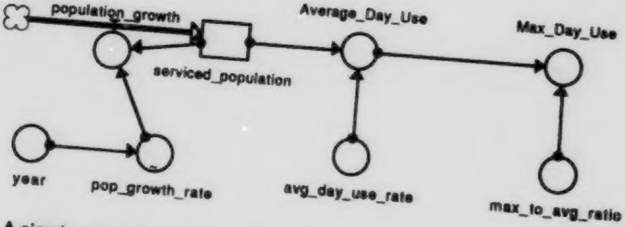

Figure 1. A simple model for forecasting water demand.

In STELLA, all inputs from one element to another, whether of quantities being modelled or of information, are indicated graphically. For example, average day use is a function of serviced population and average day use per capita. Arrows are therefore placed to indicate this. After the arrows are placed, the nature of the dependence is qualified either by an algebraic expression, or by a graphical function. "Pop_growth_rate" in this example is a graphical function of "year". STELLA then generates an equation file automatically from the diagram. Table 1 gives the equation file for this example.

Output from a STELLA model can be obtained in tabular or graphical form of both. Using STELLA models, revised input data can be used to quickly generate revised forecasts. The numerical integration capability of STELLA makes it particularly useful for forecast modelling.

- EXAMPLE 1: REGIONAL MUNICIPALITY OF WATERLOO: WATER SUPPLY

In the Tri-City area of the Regional Municipality of Waterloo, water is currently supplied from wells. Due to growth in population and industry, the current supplies will soon become inadequate. In fact, lawn watering bans have imposed frequently in recent years in order to reduced maximum day demand. A Master Water Supply Study was completed for the Region by M.M. Dillon, an engineering consultant, in 1987. The Master Water Supply Study considered various options for future sources of water supply, and recommended an aquifer recharge scheme, which involves abstracting water from the Grand River and using it to recharge the aquifer at Mannheim. The implimentation of this scheme will involve several phases. As each phase is initiated, the available water supply will increase in stepwise fashion. Construction is well under way on the first phase.

Data from the Master Water Supply Study was used in a model of water use and supply for the Tri-City area. Such a model is ideal for the determination of when new

Table 1. Equation file from the model of Figure 1.

```
serviced_population = serviced_population + dt *(population_growth)
INIT(serviced_population) = 200.000
{Units: thousands of people}
Average_Day_Use = avg_day_use_rate*serviced_population/1000
{Units: millions of gallons per day}
avg_day_use_rate = 100
{Units: gallons per person per day}
Max_Day_Use = max_to_avg_ratio*Average_Day_Use
{Units: millions of gallons per day}
max_to_avg_ratio = 1.5
{ratio of maximum day use to average day use}
population_growth = (pop_growth_rate/100)*serviced_population
year = TIME
pop_growth_rate = graph(year)
(1986.000,3.390),(1991.000,2.025),(1996.000,2.250),(2001.000,2.575),(20
06.000,1.600),(2011.000,1.800),(2016.000,1.930),(2021.000,1.630),(2026.0
00,1.400),(2031.000,2.750),(2036.000,1.100)
```

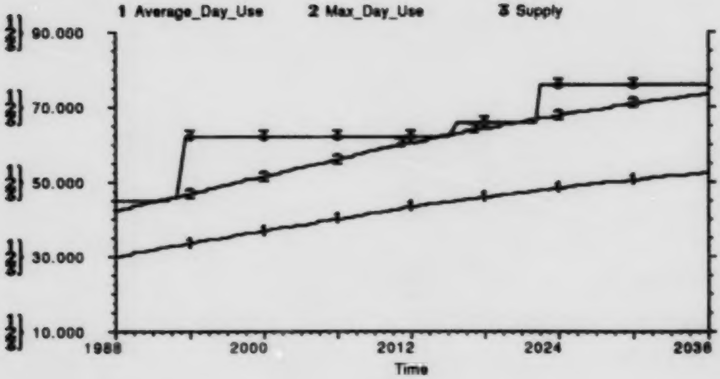

Figure 2. Water supply forecast for the Tri-City area of Waterloo Region illustrating the steps in water supply growth as controlled by maximum day use.

water supplies will be required. The word "required" used in this sense is a relative term which is dependent on the assumptions of the model with regard to water conservation options. Typical output of this STELLA model, in graphical form, is shown in Figure 2.

• EXAMPLE 2: EFFECT OF PRICE ON WATER DEMAND

The Master Water Supply Study contained recommendations for capital expenditure on water supply development which will result in increases of the real cost of water by a more than factor of three in less than a decade. The study presumed that no changes in overall water use or in the pattern of water use would result from price increases. A model was constructed to be able to evaluate the effect of price on water demand, and thus on the need to develop additional supplies. It was assumed that prices are set to cover expenses, at least in the long run. Thus demand is a function of price, but also price is a function of demand. The STELLA modelling application is particularly well suited to handling this type of mutual dependence.

Typical output of this model is shown in Figure 3. The presentation in Figure 3 is for illustration purposes only, since data on the price elasticity of water demand in Waterloo Region is not available and because in this particular model price increases occur only after capital expenditures. In practice, Waterloo Region smooths out such price increases by raising rates in anticipation of expenditures. Figure 3 shows that price increases can be expected to depress water use and delay capital expansion (compare Figure 2).

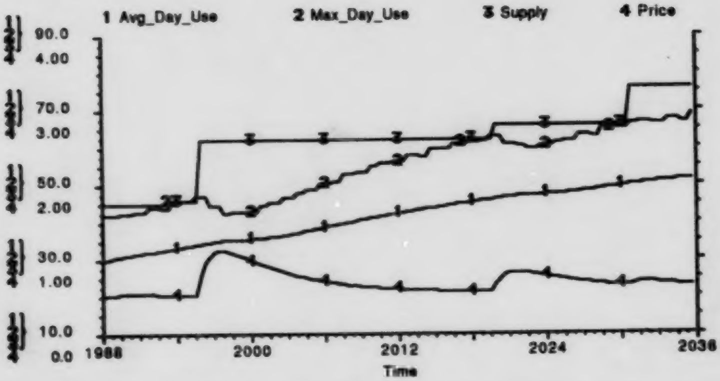

Figure 3. Water supply forecast illustrating the interrelated effects of price and water use.

• EXAMPLE 3: INTEGRATION OF WATER SUPPLY AND WASTE-WATER TREATMENT

Full implementation of the Master Water Supply Study will require abstractions of Grand River water at a rate possible only if substantial changes are made in wastewater treatment facilities. The study did not, however, consider the effects of the implied facility expansions, some of which might not be required, or might be delayed, if greater efforts at managing water demand were instituted.

In order to consider such effects, an integrated model of all water supply systems and waste water treatment systems in the Regional Municipality of Waterloo was constructed. This is the largest model to date, consisting of about 175 model elements. Because of its complexity, a custom-made user interface was designed[1]. The output of this model therefore looks different from that of previous models. A sample of its output is shown in Figure 4, which illustrates waste-water treatment of the City of Waterloo and allows comparison with water use. The excess waste-water treated at the Waterloo sewage treatment plant comes from inflow and infiltration into the sanitary sewer system. Note that the plant expansion of 1989 would not have been necessary if inflow and infiltration were reduced.

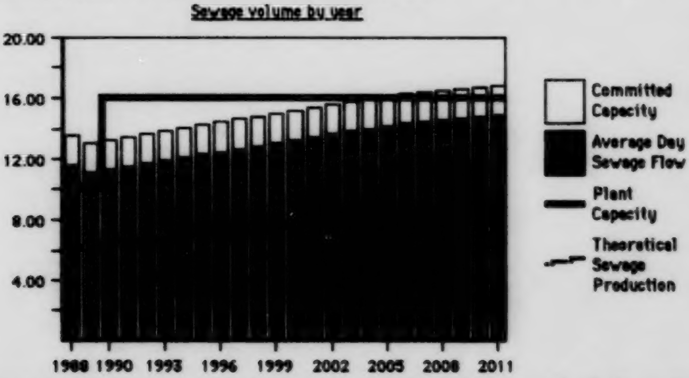

Figure 4. Wastewater treatment forecast for the City of Waterloo. All units Committed capacity refers the required treatment capacity if all approved housing units were to be built. Theoretical sewage production was set at 85% of average day water sales in the service area.

DISCUSSION

The goal of this study is to produce a model that integrates water supply with waste-water treatment in a way that promotes the use of demand management. The model is being developed to have immediate applicability in the Regional Municipality of

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[1] The interface was designed in HyperCard using STELLAStack from High Performance Systems.

Waterloo, where it would be useful for evaluating the cost effectiveness of water demand management practices and policies, as well as predicting timing of expansion of water supply and waste water treatment systems. With further development, the model could have more general applicability to municipalities across the province.

The model should be very useful both to consulting firms and to municipalities. While many people are aware of the concept of demand management, the application to water supply and wastewater treatment planning is not well understood at present. In addition, a further study to determine the effect of climate change on water demand and supply is planned.

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E8

ECONOMIC ANALYSES OF ONTARIO'S WATER POLLUTION CONTROL INITIATIVE FOR DIRECT INDUSTRIAL DISCHARGERS

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ABSTRACT

Economic analyses have played, and will continue to play, an important role in assessing the potential incremental financial and economic consequences of monitoring and abatement requirements. The purpose of the present paper is to present the results of the economic and financial analyses of the various MISA regulations that have been developed or promulgated for direct industrial dischargers, and to identify major economic issues associated with the MISA program and describe how they have been resolved or addressed with respect to industrial direct dischargers.

OVERVIEW OF THE MISA PROGRAM

The Municipal-Industrial Strategy for Abatement (MISA) program was announced by the Government of Ontario in June 1986 (MOE, June 1986), and is intended to achieve the "virtual elimination of toxic contaminants in municipal and industrial discharges into (provincial) waterways" (MOE, June 1986, p.7). To this end, regulations are being developed which require industrial plants that discharge wastewaters directly[1] into provincial waterways to monitor their effluents intensively and, ultimately, reduce the loadings and/or concentrations of certain contaminants to specified limits. These limits are to be determined according to the "Best Available Technology, Economically Achievable" (BATEA) that is specific to each particular industrial sector.

The MISA program encompasses over 300 mines and industrial establishments in Ontario which discharge their wastewaters directly into provincial waterways. These direct dischargers are disaggregated into nine industrial sectors for which monitoring and effluent Limits will be developed:

- petroleum refining
- organic chemical manufacturing
- pulp and paper
- iron and steel
- metal mining and refining
- industrial minerals and manufacturing
- electric power generation
- inorganic chemicals
- metal castings

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[1] Municipal sewage treatment plants and the industrial plants that discharge wastewaters to them will be incorporated into the program by means of several regulatory activities.

Joint Technical Committees (JTCs) have been established for each MISA industrial sector (and for municipal sewage treatment plants). These Committees are comprised of provincial, federal and industry representatives who agree upon the actual regulations. The draft regulations and other components of the MISA program are also reviewed by the MISA Advisory Committee.

A program[2] of economic investigations has been carried out in support of the MISA program and to fulfil Ontario Government requirements to evaluate the socio-economic implications of major regulatory initiatives and to provide such information to responsible Government authorities.

MISA ECONOMIC PROGRAM

A program of economic studies has been initiated to generate the required information and to complement technical assessments and regulation development efforts. The objectives of the economic program (MOE, June 1987) are:

a) to develop an economic database for those industrial sectors which will be subject to MISA monitoring and effluent limits regulations;

b) to develop estimates of the costs of proposed monitoring and effluent limits regulations for each industrial sector and for municipalities;

c) to determine the economic effects and consequences of these costs;

d) to develop criteria with which to define BATEA;

e) to design implementation programs that will achieve the MISA goals and objectives at least cost;

f) to contribute to the design of more effective policies and programs to control sewer uses by industrial dischargers; and

g) to provide information about the beneficial consequences of the various monitoring and abatement requirements including changes in the risk of certain health effects.

The economic program began with the preparation of industrial economic profiles for each sector. These profiles include physical and economic data, financial performance ratios, current trends, and forecasts of future market production and consumption trends. Following the production of these economic profiles, studies were carried out to estimate the costs of the proposed monitoring requirements for each sector and on individual firms and their plants, and to assess the economic and financial implications of these costs. These evaluations have aided Ministry personnel and the JTC in determining the most cost-effective methods of monitoring for selected contaminants. The cost of monitoring studies also identified those firms or plants which might be unduly affected by the regulatory requirements.

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[2] This program is described in MOE (1987), and Salamon and Donnan (1988).

After each 12-month monitoring period, effluent limits regulations for each direct discharge sector will be developed. Abatement technologies to achieve MISA objectives will be identified and related costs estimated for each industrial sector. A key objective will be to find combinations of technologies that will achieve the MISA objectives at least-cost and to define criteria to help judge what is "economically achievable".

EFFORTS TO DEFINE "ECONOMIC ACHIEVABILITY"

UNITED STATES EXPERIENCE[3]

In the United States, the authority to consider the economic consequences of regulatory requirements is found in statutes and executive orders, many of which apply to the U.S. Environmental Protection Agency (USEPA). Under the U.S. Clean Water Act, the USEPA rule-making activity is to establish effluent limitation guidelines for industrial and municipal wastewater treatment facilities. The Clean Water Act states that such effluent limitations will require "application of the best available technology economically achievable ...", but does not define the term. In fact, the concept of BATEA appears only once in U.S. statute, and that is in the Clean Water Act. Other environmental statutes make broad reference to economic considerations, but do not specify how they are to be measured.

While there is no explicit definition of 'economic achievability', the USEPA, based on the U.S. Congressional record and the language of the U.S. Clean Water Act, has interpreted salient Acts to mean that the primary measures of "economic achievability" for private sector regulated parties are plant closures and job loss. In practice, the USEPA has used a variety of financial measures as predictors of plant closures and job losses. Such measures differ for the private and public sectors.

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[3] This section is based on the results of a study by Peat Marwick (1990).

- 808 -

Economic impact studies of proposed regulations on private industrial sectors included calculation of the effect of incremental compliance costs on the financial statements of affected firms and, where data were available, on the cost structures of individual plants. The potential number of plant closures were inferred from these calculations.

Assessments in the United States are often tailored to focus on small business. The analytical framework is not changed, but impacts on small business are identified and the implications of less stringent control requirements for small firms are discussed.

USEPA economic studies employ a number financial ratios and cash flow analyses to estimate economic impacts. In earlier studies, the USEPA found that financial ratios can be grouped into four basic categories:

- profitability
- liquidity
- solvency
- efficiency

In its analysis, the USEPA sought to ensure that a suitable test for assessing economic impacts should possess strong empirical justification, have sufficient historical data, and can be simple and consistent to apply to available data. However, a review of sectoral economic impact studies shows that there was no consistent, rationale application of the concept of "economic achievability". For example, in the U.S. Foundry sector, firm-level financial ratios were used to predict plant closure because of the large number of plants and the resulting difficulty in gathering industry-wide plant-specific data. The three financial ratios used, which satisfied requisite criteria were: return on assets, total debt to total assets, and cash flow to total debt. Conversely in the Organic Chemicals and Non-Ferrous Metals Manufacturing sector studies, the USEPA utilized a discounted cash flow analysis.

In summary, there is no single definition or consistent application of the concept of "economic achievability" from the United States. This meant that the Ministry of the Environment must develop requisite principles, procedures and criteria to use as a framework for carrying out assessments of economic achievability for entities subject to MISA.

ONTARIO ECONOMIC ACHIEVABILITY ASSESSMENT[4]

Economic and financial assessments in support of MISA Limits Regulation development for each industrial sector will consist of four primary areas of focus. These principles and procedures are based on accepted economic theories which provide a framework for the analyses and comparisons of alternative BAT options.

Cost-Effectiveness Analyses

Cost-effectiveness analyses compare costs of different BAT (best available technology) Options with loadings of relevant pollutants to determine least-cost and cost-effectiveness of each BAT Option. Such analyses will show the distribution of costs among plants.

To the extent possible, abatement costs for relevant BAT (best available technology) options are to be estimated for individual plants subject to the MISA regulations. Types of cost information that are expected to be assembled for each sector in order to develop such BAT cost estimates include:

(a) pollutant removal efficiencies, variables that may affect the efficiencies, and operational reliability;

(b) capital costs relevant to the type and scale of each abatement technology at the plant capacity;

(c) operating and maintenance costs;

(d) operating life of abatement technologies; and

(e) private benefits of each BAT option, including reduced energy or materials inputs, saleable by-products, reduced labour requirements, and enhanced production efficiencies.

In order to compare or to sum net costs among plants, cost estimates will be converted to either annualized costs or to discounted present values. Such conversions permit one-time capital expenditures for equipment that lasts for a number of years to be considered simultaneously with annual operating and maintenance expenses.

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[4] As a prelude to the development of Limits Regulations, the Ministry identified 18 "issues of concern" and established committees comprising Ministry staff, stakeholder agencies, industry, municipalities and the MISA Advisory Committee to address these issues. The results have been published and circulated for public input. The issue of "economic achievability" is discussed on pp.97-148 (MOE, June 1990).

These cost estimates will be displayed as abatement cost functions, which are relationships between different levels of contaminant removal at a pollution source and the minimum cost of achieving them. Abatement cost functions generally display only the least-cost combinations of technologies to achieve specific degrees of removal or final loadings. The least-cost combination of compatible abatement technologies to achieve a given degree of pollutant removal is a "cost-effective BAT option". The development of up to four BAT options (i.e. four levels of water pollution abatement) will provide a clear range of cost-effective BAT options for economic achievability assessments.

Ability of Firms and Sector to Pass On Incremental Abatement Costs

Cost increases can be more easily passed along to consumers to the extent that a firm has a greater degree of monopoly power in its product market. Likewise, cost increases can be more easily passed back to suppliers to the extent that a firm has a greater degree of 'monopsony' power (i.e. when a buyer faces limited competition from other purchasers). In a competitive market, cost increases could be passed on to consumers in higher prices as more firms in the industry are subject to higher costs. However, if only a few firms in a market incur higher costs, owners of these firms are more likely to experience reduced profits.

Financial Impact Analyses of Incremental BAT Option Costs on Firms (and Plants) and Sector if Prices Cannot be Raised

Estimated incremental costs of monitoring were evaluated in relation to three financial indicators of subject firms:

a) return on investment or capital employed;
b) ratio of operating cost to after-tax profits; and
c) proportion of incremental capital cost to firm's historical capital expenditures.

Building on these analyses and the experience from the United States, it is proposed that financial indicators and tests applied to proposed MISA Limits requirements should be directed at assessing the consequences for plants (if data are available), individual firms, industrial sectors, and the provincial economy as a whole. Assessments should also be implemented to determine if there are disparities of effects between large and small businesses and between regions within the province. It must be noted that there are no widely agreed upon threshold ranges for any of the potential performance indicators.

Financial indicators of a firm (or plant) will be affected if the costs of abatement, in part or in entirety, cannot be passed on in some form. To the extent possible, analyses will explicitly show distribution of effects on firms (owners, employees), industrial sectors, and the provincial economy (consumers, sub-provincial regions, and small business).

Competitive Analyses on Firms (and Plants) and Sector if Prices Cannot be Raised

Competitive analyses involve an assessment of the operating costs of abatement relative to the position of the firm (or plant if data are available) and Sector in relation to domestic and international competitors.

COSTS AND IMPLICATIONS OF MONITORING REGULATIONS

ESTIMATED COSTS OF MONITORING

Estimates of the potential incremental costs to each plant subject to MISA monitoring requirements were calculated and published for each industrial sector. The reports also presented estimates of the economic and financial effects of the monitoring costs on each sector, subsector(s), and where possible, on individual firms. Publicly available information were used for these assessments. Ministry staff wrote to affected plants requesting the provision of plant-specific data with to conduct more salient economic analyses. However, the majority of plants felt that such information was proprietary in nature.

Incremental costs of monitoring consist of recurring operating and maintenance costs and one time capital and installation costs. In many instances, capital cost estimates were calculated by individual plants and supplied to the Ministry for incorporation into the economic assessments. The sectoral Regulations specified requirements for each of the monitoring activities for each plant. Cost-effectiveness of the monitoring requirements were examined by comparing the costs associated with the proposed monitoring requirements to the potential costs that would be incurred under alternative requirements. It was found that the incremental costs of monitoring would be much higher under the alternative scenarios.

Table 1 illustrates the capital, operating and total estimated incremental costs for each of the industrial sectors. The MISA monitoring requirements were estimated to cost $73.7 million in total, or an average of $307 thousand per plant. Draft versions of the cost of monitoring reports were issued for public and industry review and comment along with the Draft Monitoring Regulations. Subsequent comments were incorporated into the final versions of each report.

ACTUAL COSTS OF MONITORING

As a follow up exercise, the Ministry has developed a questionnaire, with assistance from 27 industrial representatives, in order to compile information on the actual costs and potential benefits of monitoring incurred by plants subject to the MISA monitoring requirements.

TABLE 1

TOTAL ESTIMATED INCREMENTAL COSTS OF
MISA MONITORING REQUIREMENTS

($ THOUSANDS)

SECTOR	# OF PLANTS*	CAPITAL	OPERATING	TOTAL	AVERAGE COST PER PLANT
PETROLEUM REFINING	7	$1,575.0	$2,081.0	$3,656.0	$522.3
ORGANIC CHEMICAL	19	$2,812.0	$8,046.5	$10,858.5	$571.5
IRON & STEEL	7	$5,120.9	$3,250.2	$8,371.1	$1,195.9
INORGANIC CHEMICAL	22	$1,485.7	$4,106.1	$5,591.8	$254.2
METAL MINING	67	$3,938.0	$14,067.0	$18,005.0	$268.7
PULP & PAPER	27	$3,697.2	$5,545.0	$9,242.2	$342.3
METAL CASTING	13	$535.0	$884.0	$1,419.0	$109.2
ELECTRIC POWER	27	$6,095.1	$8,515.1	$14,610.2	$541.1
INDUSTRIAL MINERALS **	51	$316.5	$1,666.6	$1,983.1	$38.9
TOTAL:	240	$25,575.4	$48,161.5	$73,736.9	$307.2

* Number at time of Monitoring Regulation promulgation.

** Sector contains about 130 plants. However, of the about 100 quarries, only 20 are being monitored as representative of the quarry subsector. All 100 quarries are sharing the costs of monitoring.

Source: MOE, Policy and Planning Branch

The questionnaire was distributed in June 1990 to over 300 plants subject to the MISA monitoring regulations. Participation in this exercise is entirely voluntary. Information will be received over the next year as each sector completes its monitoring requirements. To date, information has been received from all 7 plants within the Petroleum Sector.

The information collected will be used to document the actual cost and beneficial consequences of monitoring and to improve future planning and cost estimation activities. Information contained in the questionnaire will be compared with the estimated costs of monitoring in order to:

- estimate the margin of error for both capital and operating cost estimates;
- analyze reasons for discrepancies in estimates; and
- analyze the accuracy of assumptions used in the estimation of incremental monitoring costs.

Information on details such as equipment costs as a percentage of total costs, labour costs as a percentage of total costs, and an understanding of any interrelationship between costs and physical attributes (such as flow and capacity) will improve the Ministry's ability to estimate costs of concurrent and future environmental initiatives, as well as to critically review industry cost estimates. Finally, such information will provide additional background information about each plant's operation, such as the appropriate contact person, current employment levels, major products, plant capacity, and plant location.

Table 2 presents preliminary results of the estimated and actual capital and operating costs by monitoring activity for the Petroleum Sector. As indicated in Table 2, the total actual costs of all monitoring activities were 151% higher than the estimated costs. It is interesting to note that it is the reporting activity where the largest variance occurred, with the actual total costs being almost four times greater than the estimated costs.

Actual capital costs were 50% higher than the estimated capital costs, while actual operating costs were just over 40% greater than the estimated costs. These preliminary results suggest that the variance for both operating and capital costs is in large part due to the divergence of the actual and estimated costs for the reporting activity.

TABLE 2

TOTAL ACTUAL INCREMENTAL CAPITAL AND OPERATING COSTS OF MISA MONITORING
AS REPORTED BY THE
PETROLEUM REFINING SECTOR

($ Thousands)

	Capital Costs		Operating Costs		Total Costs		Percent Difference
Monitoring Activity	Estimate*	Actual	Estimate	Actual	Estimate	Actual	Actual/Estimate
Sampling	486.0	999.5	285.3	367.9	771.3	1,367.4	77%
Flow Measurement	712.0	994.2	58.0	18.2	770.0	1,012.4	31%
Analytical Testing	315.0	339.9	1,066.6	605.3	1,381.6	945.2	(32%)
Reporting	42.0	102.2	120.0	544.4	162.0	646.6	299%
Consultant Contracts	0.0	0.0	0.0	676.7	0.0	676.7	-
TOTAL	1,555.0	2,435.8	1,529.9	2,212.5	3,084.9	4,648.3	51%

* SOURCE: MOE, July 1988

Information from the questionnaire also revealed that each plant engaged at least two separate consultant contracts to perform monitoring activities for a total of 23 separate contracts for the sector. Although some consultants were hired for more than one monitoring activity, over 50% of the costs for consultant contracts were for analytical testing. The questionnaire results also indicate that only a small amount of additional employment was generated by the monitoring requirements. Just 3.5 permanent full time employees and 3 temporary employees were hired in the entire Petroleum Sector to aid in fulfilling monitoring requirements.

The only beneficial effects noted was that computer equipment purchased for monitoring could be used for other activities.

COST ANALYSES OF BAT OPTIONS FOR THE ONTARIO PETROLEUM REFINERY SECTOR[5]

Preliminary capital and operating cost estimates and pollutant removal efficiencies of specific pollution control technologies[4] for each plant in the Petroleum Sector have been prepared. The cost estimates were adjusted to each refinery on the basis of the average recorded flow rate recorded during the monitoring period. These cost and pollutant removal estimates are illustrative and do not necessarily represent the technologies that will ultimately determined to be BAT.

The application of two sets of BAT Options to each refinery show that the potential capital costs of applying the two available BAT Options range from $0.6 million to $42 million per plant while incremental O&M costs could range from $0.3 million to $3.5 million per year. Total capital costs for the Sector range from $125.5 million to $130 million. Total annualized costs, over 10 years, could range from $25.2 million to $27.2 million. These wide ranges in potential costs among each refinery are the result of the wide range of flows and contaminant levels found in effluents in each refinery.

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[5] This section relates to preliminary analyses contained in VHB (forthcoming). Cost estimates will be refined pending subsequent studies.

[4] These estimates are based on 3 potential Petroleum Sector-specific BAT Options (end of pipe filtration technologies): GMF (granular media filtration), GAC (granular carbon adsorption), and PAC (powdered activated carbon) filters. (VHB 1990) notes that these technologies will remove only 8 parameters: oil and grease, total organic compounds (TOC), total suspended solids (TSS), zinc, chromium, benzene, phenols and toluene.

The analyses indicate, taking into account some uncertainty regarding technical removal efficiencies, that the GAC-GMF BAT Option is more cost-effective in that it potentially removes more kilograms per year of all pollutants from the refineries than the PAC-GMF BAT Option.

The analyses is complicated by the fact that each BAT Option removes different pollutants at different levels of abatement. This makes defining and setting Limits difficult. One approach would be to define the best potential loading reduction achieved by each BAT Option in each refinery as the Limit. This means that each refinery would be in compliance as long as it achieves the best reductions permitted by the BAT Options for each contaminant that is possible at the particular refinery. Another approach would be to set the individual contaminant loading Limits and the lowest achieved by an Ontario refinery. This, however, may not be achievable for each contaminant of concern.

A third option is to define the Limit in terms of loadings per unit of production. A Petroleum Sector Limit would be defined as a maximum loading of a contaminant (in kilograms or tonnes per unit time) per cubic metre of crude oil processed. This definition would allow for the large differences in crude processing capacities of Ontario refineries.

As noted, these analyses are illustrative and indicate the types of analyses that will be carried out during the development of the MISA lImits Regulations. It should be emphasized as well that other important factors will also be considered in the final determination of Limits and other regulatory requirements.

CONCLUSIONS

Economic assessments will continue to be an integral part of the MISA and other Ministry environmental policy initiatives. Financial and economic analyses to-date indicate that these costs will not likely compromise the economic or financial viabilities of the sectors or the individual firms for which financial data were available. Concurrent studies (Hickling 1990, Ernst & Young 1990) have further indicated that Ontario's environmental agenda poses no major competitive disadvantage vis a vis other jurisdictions.

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The Impacts and Effects of the Hagersville Tire Fire

Preliminary Analysis and Findings

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BACKGROUND

The Hagersville tire fire broke out in the early hours of February 12, 1990. Between 13 and 14 million tires burned for seventeen days before the fire was successfully extinguished on February 28, 1990 after remarkable efforts on the part of local, regional and provincial firefighting crews. The immediate concerns of environment officials were to assess and control the effects of air-borne pollutants which had settled on local fields and bodies of surface water and of contaminants seeping through the bedrock into the groundwater feeding local wells. Concurrently, health officials directed attention to the possible immediate health risks for exposed inhabitants and to the long-term safety of the water and local agricultural produce.

During the course of the fire, initial contacts were made between local health agencies (Adult Mental Health Services and Haldimand-Norfolk Regional Health Department) concerning crisis intervention to be offered to people suffering stress as a result of the fire, evacuation and contamination. Subsequent discussions, in conjunction with the development of the joint community-Ministry of Environment Public Liaison Committee, led to the creation of the Hagersville Community Outreach Program (HCOP) to assess the psychological and social impacts of the fire on the population within a three kilometer radius of the fire site.

Shortly before the fire, the Ministry of Environment had funded our McMaster research team to examine psychosocial effects in populations exposed to environmental contaminants. The events at Hagersville prompted a supplementary study designed to examine these effects in the population affected by the fire. In so doing, the McMaster team worked in partnership with the HCOP serving as consultants in various phases of the outreach program.

THE MCMASTER STUDY

The objectives of the McMaster study were:

1. To identify the awareness and prevalence of psychosocial impacts among exposed individuals, social networks and communities.
2. To identify the coping strategies used or intended by individuals and social networks.
3. To examine the effects of locational and socio-demographic factors on awareness, psychosocial impacts and coping strategies.
4. To describe the links between awareness, experience and impacts of exposure to environmental contamination.
5. To examine the role of community context on awareness, psychosocial impacts and coping strategies.
6. To document the goals, origins, composition and patterns of influence of social networks and interest groups.
7. To examine and evaluate the impacts upon, and coping strategies used by, the workers on the fire site, including volunteers and ministry personnel.
8. To examine and evaluate the approaches adopted to communicate and consult with the local community regarding their concerns in the wake of the fire.

This paper addresses objectives 1, 2, 3, 5 and 8. The primary data used for this come from depth interviews with 43 residents from the area directly affected by the fire. The context within which the interview data need to be understood is provided by a community profile of the Hagersville area. The paper is structured in the following way: the socio-economic characteristics of the site enumeration areas (EAs) and the research evidence on stress and rural communities are presented. This is followed by a brief description of the research design and then a synthesis of the accounts provided by the residents.

COMMUNITY PROFILE

A community profile was created to provide (1) a general overview of the population surrounding the tire fire site and (2) possible baseline information relating to psychosocial impacts and coping mechanisms for environmental stress. The profile was constructed using secondary sources: census data from Statistics Canada for the seven enumeration areas (EAs) proximate to the site.

The area is predominantly rural. The population of the seven EAs is just 2100 located in scattered dwellings and in the small settlements of White Oaks, Nober, Villa Nova and Springvale (Map 1). Relative to the province as a whole, the area has a relatively stable population with a higher proportion of husband-wife families, a higher percentage of children, and a lower level of educational attainment (Table 1). It has a relatively less affluent, blue-collar population, but one in which there is a high level of private property ownership. The sociological literature would characterize such a population as generally conservative and inward-looking.

The rurality of the Hagersville population and its socio-demographic profile have implications for possible responses to stressful events. Several factors imply an enhanced capacity to cope with stressful situations. These include: the stability of the population (Lazarus and Folkman, 1984); the rural context, social structure and lifestyle (Tremblay and Anderson, 1970; Fuller, 1985; Sim, 1988); the conventional family structure (Cobb, 1976; Eyles and Woods, 1983; Hodge and Qadeer, 1983); and, following from the previous characteristics, the potential for well-developed social and community support networks (Bromet et al., 1982; Cebota and Beat, 1985; Hodge and Qadeer, 1983). But rural communities have changed and are changing and, as Hodge and Qadeer (1983) point out, familiarity in small communities does not necessarily lead to the presumption of friendliness, sociability or assistance.

Other dimensions of the socio-demographic structure in the Hagersville population imply greater susceptibility to environmental stress. These include the high percentage of households with children, the relatively low socio-economic status of area residents and the high proportion of home owners. Families in early stages of the life cycle are likely to be sensitive to environmental stress (Levine and Stone, 1986; Richardson et al. 1986). Studies by Dohrenwend et al. (1981), Kessler and Cleary (1980) and Kessler (1982) indicate that those in lower status groups are more likely to develop symptoms of distress. Homeowners are also more likely to be affected by psychosocial impacts than renters (Levine and Stone, 1986).

In summary, when compared with the evidence in the literature, the rural situation and socio-demographic attributes of the Hagersville population are such that a diversity of reactions to the tire fire could be expected with different sub-groups experiencing different levels of stress, access to support and resources and therefore capacities to cope. This anticipated diversity of responses implies the need for a research design and methodology capable of capturing a quite complex set of individual and group experiences.

THE STUDY OF ENVIRONMENTAL STRESS AND QUESTIONS OF RESEARCH DESIGN

Conceptual, contextual and practical considerations affected the choice of the research design for the Hagersville study. Conceptually, conventional epidemiologic studies of environmental stress give little attention to the roles of community context and systemic properties such as social support, value-system, health care availability in enhancing or militating against stress (Taylor et al., 1989). Contextually, the community profile recognises the potential significance of these factors in the Hagersville situation. Further, there are practical constraints on the type of research design that could be adopted. First, the potentially affected population as defined by evacuation zone is quite small, about 1300 to 1400 people (adults and children) in some 300 households. Secondly, given the nature of the event, this population was potentially traumatized with feelings of loss, distress and dislocation. An epidemiologic survey was therefore inappropriate and unfeasible. The entry of the research team into the community had to take full account of what already existed in terms of community and provincial support structures as a result of the fire. It had to be fully aware of the sensitivity of the situation so that the research would not be perceived as being an external intrusion on a local disaster. To these ends, the research process was constructed as a partnership not just between the research team and the MoE as funders but also between the team and the community by working in close collaboration with the PLC and HCOP. The sample for the McMaster study was recruited from the families who received home visits. It was, however, doubly selected, being drawn from those families (n:166) who agreed to a follow-up. We talked to 43 households and their stories form the basis of our account of the impacts of the fire. These 43 do, however, provide a cross-section of people within the evacuation zone, some being upwind of the fire, some in the red zone, some on the neighbouring concession lines and some downwind but further away.

Given these conceptual, contextual and practical considerations, we opted for depth interviewing as the primary research method. Depth interviews, and their containing suite of methods, qualitative techniques, seek to learn about the world in ways which do not rigidly structure the direction of enquiry and learning by using simplifying, acontextual and a priori definitions (Jones 1987). A depth interview is a conversation which allows the informant to relate in his/her own terms experiences and attitudes that are relevant to the research problem. It allows the researcher to probe deeply, uncover new clues, open up new dimensions of a problem and secure vivid, inclusive accounts based on personal experience (Burgess, 1982). Conversation flows in directions which the respondents want it to go. The interviewer is, however, armed with a checklist of topics that must be covered in some order and way with all respondents (Appendix 1). All the interviews in the present research were taped and transcribed in full to provide the working documents for interpretative analysis.

THE IMPACTS OF THE HAGERSVILLE TIRE FIRE: PRELIMINARY ANALYSIS OF RESIDENT ACCOUNTS

For many, the short-term effects of the fire, evacuation and their aftermath were uncertainty, confusion, distress, anxiety, inconvenience, a concern over health and a sense of loss. Our research interviews were carried out in May so people had time to reflect on what had happened to them during those 17 days in February. Things had also continued to happen to them and so when they were asked about how they cope(d) and what were (are) their worries and concerns we obtain a complex picture which relates not only to the fire and evacuation but also to the clean-up as well.

Coping requires an information base so people can decide what to do. For most, information came from the mass media. In the main, people thought that television provided the most useful and trustworthy information, probably because of the salience of this particular medium in people's everyday lives. While most of their information came from TV, radio and newspapers, they were often able to compare the written or televised accounts with their own experiences. The reported messages were often found lacking, particularly those in newspapers, the stories in which were sometimes seen as sensationalized, trivialized, acontextual or just plain wrong.

Information also came from particular provincial ministries. Those who farmed or had livestock were particularly impressed with the ways in which the Ministry of Agriculture went about its job of gathering and disseminating information and monitoring the quality of produce leaving farms. This information was believed and certainly lessened anxiety (particularly about livelihood). The same cannot be said for the Ministry of the Environment, which had to deal with all the residents and not just farmers. Further, the issues with which the MoE had to deal were wide-ranging and of immediate import to quality of life. While most residents recognized the difficulty of the work undertaken in terms of site clean-up and soil and water testing, there was a lack of understanding when technical data were presented and a general lack of trust, a theme to which we shall return.

The providing of information is a community-level response which may enhance coping capabilities. Other such responses include existing and created support mechanisms. Most people saw the role of the regional government and their local politicians as at best minimal and at worst non-existent. While provincial politicians were not seen in the area, it may be that the regional government is criticized unfairly in that its officers were active but were not perceived to be regional officials. So there was general praise for the on-line officials, particularly at the response centre in Townsend. Those manning the centre were seen as helpful in giving advice, passing people on to the relevant agency, acting as liaison with other bodies and so on. But the specially created mechanism (the HCOP) to see what help people required, to let them tell their stories, to assist with coping was poorly perceived. The research interviewers had often to probe people's responses about the HCOP. Few seemed to know of its existence, although all of our respondents would have been visited by a HCOP volunteer. Some regarded it as a waste of time and money, being an agency likely to increase rather than decrease stress and anxiety by simply asking if people had any worries. In the residents' eyes, the HCOP was not so much a failure as a non-event, something to be pushed to the back of the mind or that was irrelevant to their needs.

How then did people cope? In sum, they coped by themselves or thought that there was nothing really to cope with. Not surprisingly, the family, both immediate and extended, was used as a major resource when people required accommodation and other forms of assistance. Further, many of the anxieties and uncertainties were played out within the family unit. Husbands, wives, partners and children were reciprocally used as sources of support to militate against stress, to talk through problems and so on. Such intense, stress-related interaction was not always positive. Members of the same family disagreed about how to deal with anxieties, what certain things meant and how the unit should respond. Some existing tensions were exacerbated by having to respond to the fire and the clean-up. These difficulties and intensities were found especially amongst those closest to the fire site.

Others thought that there was little need to cope. Their lives had been disrupted for a few days, but all had returned to 'normal'. Coping thus really meant the continuous and incremental adjustment to changing life circumstances. The fire was only one element in these circumstances. And such adjustments were 'natural'. So once the fire and the worst of the clean-up had been lived through, life had to go on as it had before: work had to be carried out, children looked after, the home tended. There is a hint of fatalism or stoicism in such a response which is in some respects close to the 'rural mentality' discussed in the community profile. This conservatism, particularly one used to dealing with crises, seems well-adapted to coping. Those who were relative newcomers to the area did not always share these responses, but also tended to rely on themselves and their extended families (often in Hamilton) to cope.

We examine next longer-term impacts which have arisen through people having to live with and adjust to the effects of the fire. These relate to financial and livelihood concerns, social and community impacts, health effects and environmental impacts.

Compensation has become a divisive issue in the community. Understandably, the MoE was able to process small claims for out-of-pocket expenses caused by the evacuation and minor damage claims more quickly than major claims. All residents were satisfied with compensation for the evacuation, although it often resulted in uneasy feelings inside the extended family as the evacuees had to demand that their relatives bill them for food and accommodation. Very few people thought that the MoE should compensate them for any stress or anxiety that they suffered during the fire or evacuation and their aftermath. Major claims for damage to homes and goods and for buying out those who feel that they cannot return to their homes have not been processed quickly. There is widespread resentment at the speed of processing. This resentment is exacerbated by the perceived insensitivity with which the MoE rehoused those who cannot go back. They were housed in trailers near Townsend. Some families have spent up to six months in these cramped conditions. They firmly believe that there are vacant Ontario housing dwellings to which they could have been moved.

Part of the negotiations for the compensation package involve valuing the home and lot itself. There have been disagreements on these values, mainly because there are few similar properties in the area (and fewer recent sales) and because of a depressed market. In fact a dominant theme among the respondents whatever their location was worry about the impact of the fire on property values. They felt that few outsiders would be willing to buy in the area and if they were it would be at reduced prices. Many conceded though that the impact on property values would be a more short-term effect. The fire and clean-up would soon receive no media coverage and would no longer be in people's mind. In the long-term, it was thought property values would not be affected, although much would depend on the efficacy of the clean-up operations.

The farmers were also concerned about marketing their produce, fearful that their wholesalers would refuse to accept goods or livestock that came from the Hagersville area. The Ministry of Agriculture had set up produce testing for which the farmers were extremely grateful. In the longer-term, they felt their livelihoods would be more affected by the vagaries of the market. Those with seasonal crops were more worried as were those with businesses that relied on positive public perception e.g. dog kennels. All those with farming or livestock business were however concerned about water and its quality, whether in terms of accessible potable water or of fencing off creeks and water bodies that may be affected by pollutant run-off.

Few social or community impacts were reported by the 43 households. Indeed one of the main themes to emerge is the isolation of the family unit, which points up a changing rural scene. Few felt that the community as community was affected at all by the fire or evacuation. There was a brief coming together during the fire itself and for the first public meetings, but after that most simply and perhaps understandably wanted to get on with their own lives and get those back to 'normal'. Indeed, it was the potentially divisive dimension of compensation rather than community spirit that was mentioned. Further, respondents would refer to the strains on the family of getting lives back together, especially if they had been evacuated. More likely, especially in areas west of Townline and in White Oaks, people wondered what all the fuss was about especially after the plume had disappeared.

Few were concerned then about the health effects of the event. Few saw their physical or mental well-being affected by the fire. Mental well-being did not emerge as a significant theme, except in the short-term and among those households who would not return to their homes. In fact, physical well-being seemed more likely to arise as an anxiety, particularly for respondents' children over whom there was a vague unease about future diseases. There were also vague but general worries about the health of all if the water supply in the area had been adversely affected by the fire and the clean-up.

The fourth theme refers to environmental impacts. Worries about air quality were short-lived but virtually everyone is concerned about water quality. There is fear about the effects of the toxic run-off from the site. This run-off has mainly been collected at a water-treatment plant adjacent to the site but some polluted water has percolated into the groundwater. There is uncertainty in which direction and at what rate this water and the heavy oils and metals from the melted tires will run. If the process is slow, it may be years before the full consequences are known. The December 1991 deadline for long-term compensation is, therefore, regarded as inappropriate. There is also general dissatisfaction about water quality testing that has been and continues to be carried out by the MoE. The site has been ringed with test wells to monitor for toxins and pollutants, but most are dissatisfied, wanting their own well water to be tested.

While water quality is the dominant long-term impact from the residents' point of view, water-testing may also be used to illustrate their attitudes towards government, which in this final set of comments will be linked to reflections on 'causes' of the fire and accountability. There is a widespread mistrust of government, which most probably emanates from general economic and political life in the region and the province. With respect to the fire, government is seen as insensitive, uncoordinated, slow and uncaring. Parts of its apparatus are viewed positively (e.g., the response centre, Agriculture's involvement and testing, particular on-line MoE workers and officials), but many hold government in contempt not only for the clean-up difficulties but also for allowing the fire to happen in the first place. In fact, few blame the site owner for the fire. He is primarily seen as a businessman trying to earn a living but constrained by government and court inaction. Some saw him as fulfilling a community need by taking the tires. There is a degree of fatalism in some resident's views on causation. The site was seen as an accident waiting to happen. It was inevitable that something would occur, although it must be added the site did not loom large in people's pre-fire minds. The pile was simply part of the landscape. But it was a pile for which the government is held largely accountable in that its various agencies should have listened to Straza's petitions more attentively, policed him more effectively, ensured speedier court action and used the tire tax monies to set up recycling capacity. The government is held accountable then for the circumstances that allowed the fire to happen, not of course the fire itself. Although with the fire, the government is not completely absolved. There were comments that the Young Offenders Act and the probation service were not tough or efficient enough. The youths, who allegedly started the fire, are seen merely as the literal and metaphorical spark. Many though believe that they were native youth and although some recognize that natives suffer many deprivations, stereotypical, racist explanations were employed. With respect to causation, we again see the fire as a potentially divisive force in the community. But overall in terms of accountability, the government is less highly regarded by those in the Hagersville area than it was before.

PRELIMINARY RESEARCH CONCLUSIONS

Three major sets of themes emerge from this preliminary analysis of the resident interviews: the evacuation and its immediate aftermath (only briefly mentioned in this paper); the coping strategies employed and the role of information in coping; and the impacts of the event (economic, community, health, environmental) and the effects of these on attitudes to government through the notion of accountability.

Most residents were aware of the possible effects of the fire but there was a low prevalence of psychosocial impacts. More important were economic and environmental anxieties (objective 1). Further, there were some locational and length of residence variations in impacts (3). For most, however, community appeared to be relatively unimportant (5), while families were the main resources for coping with the fire and evacuation (2). Even the specially created HCOP was not regarded as important, although for consultation purposes, the response centre was highly regarded (8). It is though possible to suggest that community context, defined in terms of rurality and farming, may have shaped the nature of the responses (5). But the 'invisibility' of the disaster meant that after the fire was put out the perception of risk was quite low and mainly concentrated among those who had lived close to the site.

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Site Location: Hagersville Tire Fire

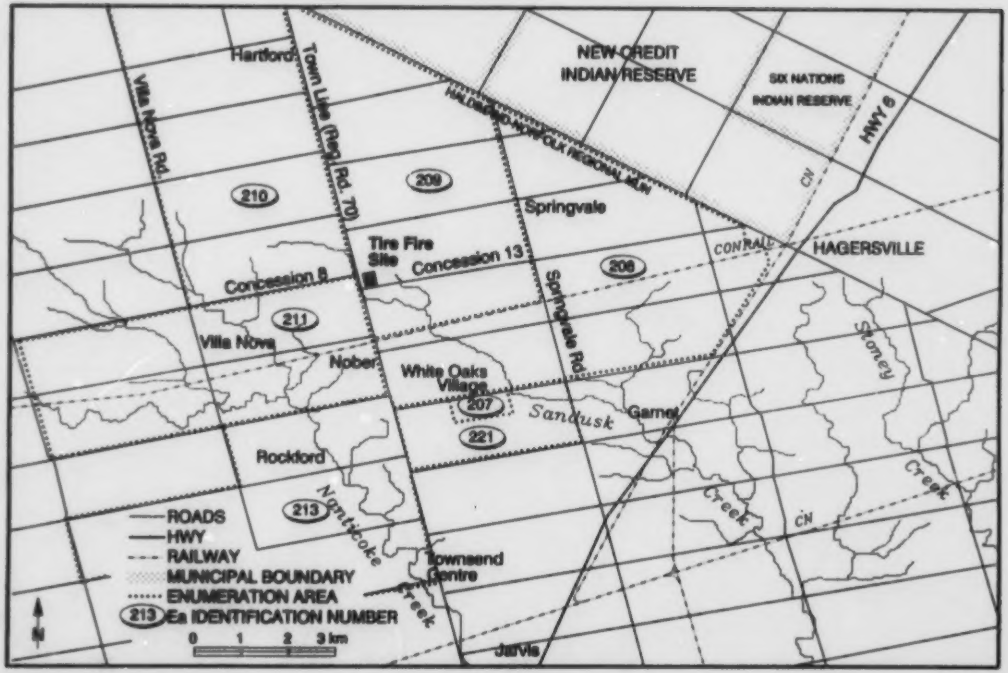
NEW CREDIT
INDIAN RESERVE
SIX NATIONS
INDIAN RESERVE
HWY 6
CN
HALDIMAND-NORFOLK REGIONAL MUN
HAGERSVILLE
CONRAIL
Hartford
Town Line (Reg. Rd. 70)
Villa Nova Rd.
210
209
206
Springvale
Tire Fire
Site
Concession 13
Concession 8
211
Villa Nova
Nober
White Oaks
Village
207
221
Springvale Rd.
Stoney
Sandusk
Garnet
Rockford
213
Nanticoke
Creek
Creek
Creek
CN
Townsend
Centre
Jarvis
ROADS
HWY
RAILWAY
MUNICIPAL BOUNDARY
ENUMERATION AREA
213 Ea IDENTIFICATION NUMBER
0 1 2 3 km
N

Table 1
Selected Population Characteristics 1986: Ontario, Haldimand-Norfolk, Site EAs

Characteristic	Ontario	H-N	Site EAs
% population change (1981-6)	5.5	0.7	n.a.
% non-movers (1981-6)	55.5	64.9	69.4
% aged 14 and under	20.5	22.5	27.1
average no. of children per census family	1.3	1.3	1.5
% aged 65 and over	10.9	12.6	7.6
% single aged 15 and over	21.1	17.2	13.4
% married	50.8	52.8	49.8
% husband-wife families	88.1	90.9	91.2
% lone parent families	11.9	9.2	8.8
% less than grade 9 education	14.6	15.3	19.9
% university with degree	10.8	3.5	3.8
% primary occupations (male)	2.7	10.9	18.8
% machinery, fabrication, assembly and repair (male)	8.9	10.0	8.7
% service (female)	6.3	5.8	5.2
% sales (female)	4.2	3.4	2.2
% managerial (male)	7.4	4.9	3.5
average household income ($)	38022	31812	33438
average dwelling value ($)	104063	71648	88846
% owned dwellings	63.6	74.5	70.9
% single detached house	57.4	83.9	96.1

Sources: Statistics Canada 1987, 1990.

APPENDIX 1: INTERVIEW CHECKLIST
HAGERSVILLE TIRE FIRE

(1) How did the fire and resulting evacuation affect you?
How did it affect your family? How did it affect your friends?

(2) Why did all this happen here? Why would it happen here?

(3) How did you and your family cope?
Have others helped you out, or have you helped others? If so, how?
PROBE: family
friends
professionals - health, social, others
church
community groups
local and/or provincial government
others
Are your contacts/ties better or worse as a result?

(4) What do you think about the job done by the:
- firefighters
- local officials
- provincial officials (especially MoE)
- media
- outreach program
- others?

(5) During the fire and evacuation there must have been alot of information (and rumours) going about. What sources of information about the fire and related events were important?
Were you happier with some sources more than with others? Which ones?
Did you have more trust in certain information sources than in others? Which ones?

(6) What really worries you now?
PROBE: own health
health of children
livelihood
property values/image of community
compensation
environmental quality (water, air)
What do you think will really concern you in three months time?
What about in a year's time?
Do you have any other worries?

(7) Has the fire and its aftermath changed you?
your family?
your friends?
For better or for worse?

(8) Have you lived in this area most or all your life?
If not, when did you move here? Why?
What was good about living here?
What's been difficult in living here?
Have they changed? Will the community be the same again? Why/why not?

(9) Do you plan to remain in this area?
Is there anything that can be done for you and the community?

VOLUME II

SESSION F

MULTIMEDIA CONTAMINANTS & BIOTECHNOLOGY RESEARCH

VERBAL PRESENTATIONS

P2

Regulating a Multi-Media Contaminant: US EPA's Lead Strategy

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Lead contamination of the industrialized world is ubiquitous and current levels are 1000-fold higher than background, natural levels. Lead contaminates every environmental compartment: air, surface and ground waters, soil and dust, and each compartment is a potential pathway of human exposure. The current literature shows evidence of lead's health effects at lower and lower exposure levels, indeed, at levels previously considered 'safe'.

The US Environmental Protection Agency (EPA) considers lead to be the nation's most toxic multi-media contaminant. It is a significant health problem, primarily because of its impact on infants and children, but also because of its effect on pregnant women and even adult males. EPA is also concerned about the ecological impacts of environmental contamination from lead.

Lead as a Multi-media Pollutant

Lead has hundreds of commercial applications, including as an octane-booster in gasoline; in radiation shields and sheathing for cables; in solder used in plumbing, stained glass and electronics; in pigments for ceramic glazes, paint and newspaper ink; in fine crystal; in pesticides and plant growth regulators; and in hair preparations. Elemental lead is used for water pipes and fishing weights, curtain weights and weights for divers. By volume, most lead is used for automobile batteries.

Each year about 1.2 million metric tons of lead are used in the US and the amount of lead introduced into commerce annually has remained relatively constant for the past 10-20 years, although usage patterns have changed dramatically. The change has occurred primarily because gasoline lead levels have declined by over 98% from the early 1970's to the present, while the number of automobile batteries made and the amount of lead used in them has increased, offsetting the decline in leaded gasoline. Some other sources, such as lead used in solder for food cans, represents a fairly trivial amount of lead by volume, so the recent decline in usage has been almost imperceptible in total lead consumption.

Exposure does not necessarily equate to use. As examples, leaded gasoline was a major use of lead and a major exposure source. Lead in solder in food cans was a trivial use by volume but a significant exposure source. Lead in automobile batteries has been a source of occupational exposure to workers and a major environment pollutant for their families and those in the vicinity, but the use of lead batteries is not a significant exposure source to the general population. Etc.

Blood lead levels in the US have decreased by more than half between the mid 1970's and the late 1980's due to the phasedown of lead in gasoline and reductions in dietary lead. These reductions have had a great effect both on the general population and on populations at-risk of toxicity from specific sources. The principal remaining exposure sources for the general population are drinking water, food, combustion of leaded gasoline, industrial emissions, and soil and dust (interior and exterior) contaminated in the past or present by leaded gasoline and lead-based paint. The principal sources of lead toxicity in children is lead-based paint, followed by drinking water, contaminated soil and dust in urban areas and from the lead industries (smelting, mining and refining), and a host of localized problems such as other occupational exposures (electronics, PVC pipes, munitions, etc.), folk remedies, dietary exposures, hobbies, and even make-up.

At the same time that blood lead levels have been falling in the US, we have been finding that adverse health effects occur at lower exposure levels, indeed, at levels previously thought to be "safe." So the lead problem remains to be "solved".

In addition to the risk of human exposure, lead contamination is also an ecological disaster in much surface and ground water, in huge tracts of land, and appears even in the deepest oceans. Lead is phytotoxic and causes adverse effects in aquatic and terrestrial species. Elemental lead has a very long half-life, and evidence from the Periclean silver mines in Attica and from Roman installations in England suggest that environmental lead pollution does not disappear quickly.

EPA's Regulation of Lead

EPA's regulation of lead began in 1973 when EPA began to restrict the amount of lead used in gasoline. This was done to assure the availability of unleaded gasoline for vehicles with pollution-control devices (catalytic converters) that are fouled by leaded fuel and to reduce exposure to lead. Since then, EPA has further restricted the use of lead in gasoline, and overall combustion of lead in gasoline has been reduced by about 98% in the past 17 years.

In 1978, EPA set a National Ambient Air Quality Standard (NAAQS) for lead, which is 1.5 ug/m^3 averaged quarterly. This is still the U.S. ambient air standard, although lead levels in most cities average about 0.1 to 0.4 ug/m^3 or 10-20% of the NAAQS. The only places not now attaining the 1978 NAAQS are probably several areas directly around some smelters and battery plants; however, not all stationary sites currently have proximate air monitors. EPA is in the process of re-evaluating the NAAQS and will also likely require the installation of more air monitors in areas at risk of high air lead levels.

The Maximum Contaminant Level (MCL) for lead in drinking water was set in 1975, but EPA merely adopted the standard set by the US Public Health Service in the 1960's. By convention although not by regulation, the MCL is measured in fully flushed water -- that is, the sample is taken after the water has been running for 2-3 minutes. EPA has proposed to significantly lower the allowable level for lead in US public drinking water. To better protect against exposure to elevated lead levels, it is likely the standard will apply to water that has been sitting in household pipes for 6 hours or more. EPA will probably publish these regulations by the end of 1990.

EPA regulates discharges to surface waters through 2 mechanisms: water quality criteria and industry-specific effluent guidelines. Twenty-three industrial point source categories now regulate the discharge of lead in their waste waters and effluent standards for 2 additional categories (pesticides, and paper and pulp) are being developed; ten new categories are being considered for regulation. Water quality criteria consider the protection of human and aquatic life, recreative uses and aesthetics. Industry-specific effluent guidelines should assure that general water quality standards are not exceeded. The criteria for lead are

	maximum concentration †	average concentration
Freshwater	82 ug/l*	3.2 ug/l*
Salt water	220 ug/l	8.5 ug/l
Human health	50 ug/l**	50 ug/l**

In EPA's hazardous waste programs, wastes are regulated based on their potential to leach lead to ground water. Our waste disposal program, under the authority of the Resource Conservation and Recovery Act (RCRA), requires that solid waste sufficiently contaminated with lead must be disposed of in a permitted hazardous waste disposal facility that is operated so as to protect human health and the environment. The basis for the "tox numbers" used for design, operation, closure and cleanup of hazardous waste facilities are typically Reference Dose values (RfD's) or cancer risk numbers, or in the absence of these numbers, background levels of lead. Whether or not a waste is hazardous is determined by the Toxicity Characteristic Leaching Procedure (TCLP), which has recently replaced the Extraction Procedure (EP) leach test.

Of approximately 1200 Superfund (hazardous waste disposal) sites on the National Priority List, about one-third have lead as a major contaminant. There is no EPA soil-lead standard but the general guideline set by the US Centers for Disease Control of 500-1000 ppm is widely used in clean-ups. Urban soils, which can often reach levels of 500-1000 ppm or even higher in some parts of older cities, may present a complication here.

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*Fresh water aquatic life criteria for metals are expressed as a function of total hardness (assuming 100 mg/l of $CaCO_3$).

**These numbers are based on the drinking water standard for lead and will change when a new drinking water regulation is published.

† Maximum concentrations cannot be maintained for more than 96 hours.

Finally, lead arsenate and several other inorganic arsenic compounds containing lead are under special review by EPA. The use of pesticides and fruit growth regulators containing lead will probably be voluntarily discontinued; lead arsenate has not been produced since 1985, although in 1989, 10,000 pounds was still available for use in Florida.

Coordinating EPA's Lead Activities

Officially, the development of a multi-media strategy to standardize all aspects of lead contamination, exposure, remediation and effects began in Spring of 1988, with testimony from each of EPA's program offices before EPA's Science Advisory Committee. Its framework was set in the Fall of 1988 when EPA's Office of Research and Development decided to develop a single multi-media research strategy for lead instead of independent programs to support each individual regulatory effort. The overall goals and directions of the agency's many regulatory activities for lead were established this year when EPA's Deputy Administrator called for the development of an EPA-wide Lead Strategy.

Unofficially, of course, coordination on the staff level occurred much earlier because many of the same people support lead research and regulation in the different EPA programs.

Nonetheless, developing a comprehensive lead strategy was not possible without support from the most senior levels of the agency and, of course, targeted resources. EPA, which is perceived by the US Congress as the repository of lead expertise and as an agency capable of successfully tackling large environmental problems, has received $7.5 million dollars in the past 2-3 years, specifically to address lead problems. In addition, recent legislation and language in our budget appropriations have expanded EPA's authorities and obligations for regulating lead. For instance, the 1987 Lead Contamination Control Act extended to EPA the regulation of water coolers and water fountains, and of water in schools.

EPA's Lead Strategy

EPA's proposed goal for its lead strategy is simple:

> **Reduce lead exposures to the fullest extent possible, with particular emphasis on the risk to children.**

This single goal will be achieved through 2 objectives:

1. Significantly reduce the incidence of blood lead levels over 10 ug/dl in children; and

2. Reduce insofar as feasible the amount of lead introduced into the environment, in order to afford as much protection as possible to both humans and ecosystems.

Achieving the proposed goal is limited by 2 major constraints: authority and resources.

EPA does not presently have regulatory authority regarding most of the sources of either high hazard or general population exposures. Many of the major sources of immediate hazard to children today are a legacy of past uses. These include lead-based paint on the exteriors and interior of buildings; urban soil and dust contaminated by lead from the weathering of lead-based paint; the combustion of leaded gasoline; emissions from a host of industrial sources; and drinking water contaminated primarily by lead leaching from solder used to join copper pipes, faucets (brass and bronze can both contain significant amounts of lead) and flux. Other important sources of lead exposure for the general population include cigarettes, food, occupational exposures, wine and other alcohol, hobbies, ambient air, leaching from ceramics and possibly leaded crystal, and waste disposal practices.

Exposure to in-place lead-based paint, which is probably the largest source of toxicity to children, is not effectively regulated by any Federal agency. The US Department of Housing and Urban Development (HUD) has had responsibility for abating this risk in public housing. However, because of the enormous expense associated with the abatement of this housing as well as policy and programmatic obstacles, HUD has not been able to affect much of this housing. The abatement of private housing is not controlled by any Federal agency. Dietary exposure, which may account for 20-40% of general exposure, is regulated largely by the US Food and Drug Administration. Lead contaminated urban soil may account for another 10-30% of general population exposure and is also likely to be a major source of lead toxicity for US children; no Federal agency has explicit authority to regulate background soil levels. etc.

The costs of abating these exposures are also enormous. As an example, abating one housing unit costs $3-7,000, and there are probably up to 50 million units requiring abatement. The removal or treatment of lead-contaminated soil probably costs $1-5,000 for about a half an acre. Many of the 40- 50 million housing units with lead-based paint also have high soil-lead levels, as do areas adjacent to major roadways or industries using lead. Each of these 2 problems is likely to cost about $10 billion, even if only the most severe parts of the problems are addressed.

A further complication with activities to reduce exposure to lead is that some abatement methods, particularly those related to abating lead-based paint, can actually increase exposure if not carefully and correctly done.

EPA's strategy, therefore, proposes to regulate those exposure sources and pathways under its control, conduct analyses to better assess exposure and to identify effective abatement technologies, work with other Federal agencies to address sources under their authorities, and mobilize all aspects of the public and private sectors in the effort to abate exposure to lead in the US.

Specifically, EPA's proposed strategy contains the following:

Regulatory activities: --implement a strong pollution prevention program;
--develop soil-lead guidelines;
--re-evaluate the lead NAAQS and develop a plan for bringing all smelters into compliance;
--develop New Source Performance Standards for new facilities;
--publish regulations to reduce lead in drinking water;
--publish regulations for disposal of sewage sludge to minimize lead exposure;
--evaluate the use of lead in all pesticides;
--consider using the Toxic Substances Control Act to restrict new uses of lead and/or phase-out unnecessary or high exposure uses of lead.

Coordination: --within and between EPA programs;
--with other Federal agencies;
--with state and local governments; and
--with the private sector.

Research: --accurately characterize general population and high level lead exposures;
--identify geographic 'hot spots' for lead exposure; and
--develop and transfer efficient and effective lead abatement technology.

Other: --assure the availability of environmentally sound lead recycling.

The Use of Cost-Benefit Analysis

Reducing exposure to lead costs money, in terms of reduced emissions, actual abatement or remediation, switching to more expensive substitutes, and related direct and indirect costs such as required research and development, premature retirement of capital equipment, potential industrial dislocations, etc. On the other hand, continued exposure to lead also costs money, in terms of direct and indirect medical expenses, contamination of surface and ground waters, loss of waterfowl and other aquatic species, damage to plants and the like.

In addition, because of how lead contaminants certain environmental compartments, remediation may actually have unrelated benefits. Two examples are lead contamination of drinking water and the use of leaded gasoline. Lead usually contaminates drinking water by the corrosion of plumbing materials containing lead and the subsequent leaching of lead into the water. The easiest and least expensive way to remediate the problem is to reduce the corrosivity of the water. Making the water less corrosive reduces all damage from corrosion, resulting in significant cost savings to both consumers and the water utility. Switching to unleaded gasoline provides benefits to vehicle owners in the forms of lower maintenance costs from lead-induced corrosion of exhaust systems and engines, and increased fuel economy. In addition, the use of catalytic converters unfouled by leaded gasoline reduces emissions of conventional air pollutants (hydrocarbons, nitrogen oxides, carbon monoxide).

One way to evaluate a particular action or to compare alternative action is to compare costs and benefits. Costs are generally more easily quantified than benefits and generally relate to common business uncertainties: How long will the machinery last? Will the market grow or contract over the time period considered? What will happen to interest rates? etc.

Benefits are usually more difficult to calculate and, as yet and to my knowledge, no benefit analysis has attempted (or claimed) to estimate all the benefits of a given action. Benefits usually include health and welfare improvements, public goods, decreased ecological and environmental damage, etc.; obviously, these are difficult to even describe qualitatively, let alone to estimate quantitatively. Consequently, they usually underestimate actual benefits.

EPA must decide among many alternatives for reducing lead exposure. This includes evaluating the costs and benefits of different levels for a single action (e.g., different ambient air lead levels) as well as comparing alternative actions (e.g., reducing exposure to lead in drinking water vs lead in paint). EPA often uses cost-benefit analysis where possible in decision-making.

The first major cost-benefit was done to support the 1985 phasedown of lead in gasoline. The methods developed for that analysis were expanded in 1986 and 87 to support the proposal to reduce lead levels in drinking water; the drinking water analysis is being partially redone to support the promulgation of the lead in drinking water regulation. Most recently, EPA has used many of these same methodologies to evaluate the regulation of sewage sludge, an analysis driven largely by concerns over lead.

As examples, Table 1 contains the estimated costs and some of the estimated benefits associated with the 1985 phasedown of lead in gasoline and the drinking water regulation proposed in 1986. For comparison, all costs have been updated to 1989 dollars. As can be seen, while each regulation has significant costs, each is also associated with greater net annualt benefits.

Conclusions

Developing workable solutions to the lead problem is technically very complex, and current solutions are extremely expensive, particularly when they involve abatement actions such as removing old paint, soil, or plumbing from millions of home. And if not carefully done, some abatement efforts can actually increase exposures. Further, lead contamination comes from a variety of sources that are both geographically dispersed and regulated by a wide range of federal and other entities. Finding workable solutions to the array of problems is difficult and must consider both the costs and expected benefits of such actions. Cost-benefit analysis is a tool that can provide guidance to decision-makers.

Table 1: Cost-Benefit Analysis of Two EPA Lead Regulations
(millions 1989 dollars)

	Lead Phasedown* (Gasoline)	Drinking Water Regulation**
Annual Costs	$ 760	$ 270
Monetized Annual Health Benefits		
1. Children		
Reduced Medical Costs	$ 750	$ 30
Reduced Cognitive Damage	not calculated	$ 200
2. Adults		
Cardiovascular Effects	$ 7,300	$ 340
Other Monetized Annual Benefits		
Vehicle Maintenance Benefits	$ 1,400	not applicable
Conventional Pollutant Benefits	$ 280	not applicable
Materials Benefits	not applicable	$ 610
Total Annual Calculated Benefits	$ 9,730	$ 1,180
NET ANNUAL BENEFITS	**$ 8,970**	**$ 910**

Sources: US EPA, 1985. The Costs and Benefits of Reducing Lead in Gasoline. Office of Policy Analysis. EPA-230-05-85-006.
US EPA, 1986. Reducing Lead in Drinking Water: A Benefit Analysis. Office of Policy Planning and Evaluation. EPA-230-09-86-019.

* Sample year 1986
** Sample year 1988

F3

Application of a Multimedia Risk Assessment Approach to Ontario Soil Contamination Cases.

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Introduction

Regulatory agencies are increasingly relying upon the utilization of risk assessment methodologies as a tool for the effective development of environmental management strategies. In assessing environmental health risks, whether in a site-specific or general population context, it is increasingly recognized that an integrated assessment of exposure from multiple routes is necessary to understand the total risk to the target organisms, as well as the contributory risk posed by the media in question. At the Ontario Ministry of the Environment (MOE), multimedia risk assessment is currently being applied to a number of problems. The following paper describes such as approach as applied to the question of human health implications posed by metal contamination of soils at various Ontario sites. A specific case of copper contamination is described for illustrative purposes.

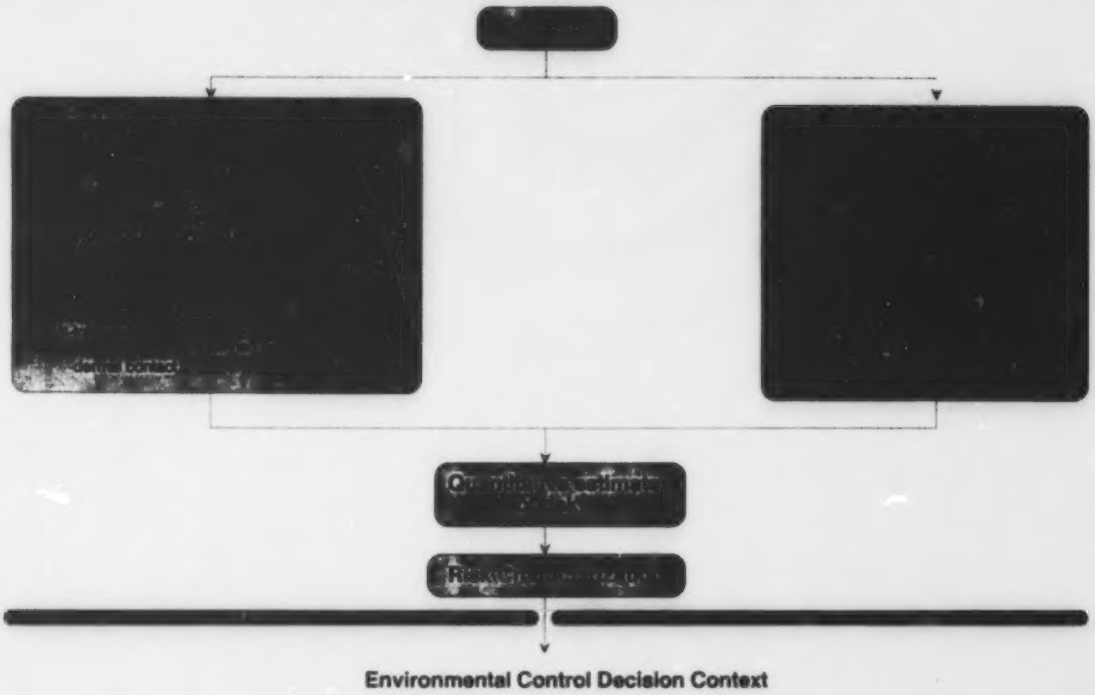
Elevated levels of copper were found in 1988-89 soil samples collected by the Ministry of the Environment on residential and publicly accessible properties adjacent to Burnstein Castings, a small foundry located in a residential neighbourhood of St. Catharines (MOE, 1990). Residential housing and a public school are located directly adjacent to the site. Quantitative risk assessment was undertaken to consider the question of whether exposure to the reported concentrations of copper in soil might pose a potential health risk to community residents.

The general approach is based upon conventional models of risk assessment (see Figure 1). The exercise consists primarily of three components: 1.) a review of the known toxicological properties and human health effects of copper 2.) development of estimates of potential exposures via multiple exposure pathways for adults and young children; and 3.) a characterization of risks from estimated exposures when compared to current exposure limits for copper.

The relative contribution of soil/dust ingestion to total copper exposure is assessed against a simplistic analysis of intake from other pathways (food, air and drinking water), which are modelled utilizing available monitoring data and various human intake assumptions for each media. Average exposures for each pathway are then integrated to provide an estimate of possible total copper intake for individuals in the area. A worst case scenario for soil/dust ingestion and the question of consumption of homegrown produce are also considered.

In characterization of risks, the calculated intakes for copper are compared against existing exposure limits of which there are basically two types: 1.) maximum acceptable daily intakes; and 2.) recommended daily intakes based on minimal nutritional requirements. Based upon this analysis,.the copper levels in soil in this community are estimated to result in exposures which are below currently recommended maximum acceptable health limits.

FIGURE 1: RISK ASSESSMENT FRAMEWORK


dermal contact
Quantitative estimate of risk
Risk characterization
Environmental Control Decision Context

Toxicological Assessment of Copper

The biology of copper has previously been the subject of a number of more comprehensive reviews (NAS, 1977, 1980; Stokinger, 1980; WHO, 1984; USEPA, 1985) and the more salient characteristics are summarized here. Copper is considered to be an essential element in the diet of humans for proper nutrition , and it is widely distributed in the body. It is involved in a variety of essential bodily processes including erythrocyte formation, the release of tissue iron and the development of bone, connective tissue and the central nervous system. In addition, Cu is necessary for the proper functioning of many enzyme systems and is associated with certain elements of blood.

Animal experiments indicate that deficiencies of copper are associated with anemia, depigmentation, depressed growth, bone dystrophies and gastrointestinal disorders.

Copper is absorbed from the lungs or gastrointestinal tract following exposure. It has the highest bodily accumulations in the brain, kidney, heart liver and pancreas. Copper appears to be excreted in the feces and at a constant rate by the kidneys. Excess Cu can be eliminated in feces with little change in the rate of elimination from the kidneys.

Although not thoroughly understood, homeostatic mechanisms in normal humans provide a balance between copper intake and elimination. It is known that serum copper levels may vary widely depending on age, sex, hormonal and nutritional status. The homeostatic mechanisms prevent toxicity from the range of normal variations in copper.

Copper is rarely systemically toxic when ingested unless very high amounts are absorbed. Acute poisoning via oral ingestion of Cu is rare due to the powerful emetic action of this metal. However, in instances of large oral exposures, effects such as mucosal irritation, capillary damage, hepatic and renal injury and central nervous system irritation have been reported. Severe gastrointestinal irritation is also associated with large single doses of Cu. Application of concentrated copper salts on the skin has led to papulovesicular eczema and other symptoms, reflecting the corrosive nature of the salts.

Airborne exposures to copper have occurred in the occupational setting. Pulmonary exposures have been observed to result in irritation of the respiratory tract, nausea and metal-fume fever. In some cases, discoloration of the skin and hair has been observed.

The scientific literature is replete with studies regarding the nutritional essentiality of copper, but copper toxicity from chronic exposure has not been well investigated. There are no data indicating that human exposure to copper results in chronic toxic effects. Diets containing up to 5.8 mg of Cu/day have produced no noticeable effects in humans. Long-term inhalation of copper fumes and fine aerosols may result in metal-fume fever. Wilson's disease (hereditary hepatolenticular degeneration), a rare inborn error of metabolism, appears to be the only manifested form of chronic copper toxicity by ingestion in humans. This is a condition characterized by bodily retention of high levels of copper, accumulating in brain, liver and kidney.Another group at increased risk from chronic high level ingestion are individuals with glucose-6-phosphate deficiencies.

There is no evidence that any copper compounds are carcinogenic. The International Agency for research on Cancer has not evaluated copper or copper compounds for carcinogenicity. Copper is classified by the U.S. EPA in the Group D, inadequate data in humans and animals.

Existing Standards and Recommended Limits for Copper

The review of the potential human health implications of copper levels in soils reported in the Phytotoxicology Assessment Surveys stem from observations of levels which exceed the MOE Upper Limit of Normal (ULN) urban guideline for copper in soil of 100 ppm. As indicated in the report, this guideline is based upon a statistical consideration of available analytical data and is not based upon health considerations. The ULN guideline itself therefore provides no comparative health risk benchmark against which to evaluate the elevated soil copper levels. It is therefore useful to consider existing guidelines for copper from other agencies. In the case of copper there are basically two types of limits to consider; 1.) Recommended daily intakes which are based on a minimum nutritional requirement and 2.) Maximum permissible intakes.

1. Recommended Daily Intakes

For children, a World Health Organization recommended daily intake (WHO-RDI) of 0.08 mg/kg body weight (1.2 mg/day for a 15 kg child) is thought to be necessary for proper development.

The National Academy of Sciences (1980) has a recommended daily allowance (RDA) for copper of 2.0 - 3.0 mg/day for adults and 1.5 - 2.5 mg/day for children. The 1980 estimated safe and adequate daily dietary intake (ESADDI) ranges for the adult diet is 2.0 - 3.0 mg/day; the ESADDI ranges for the infant and toddler diets were 0.7 - 1.0 mg/day and 1.0 - 1.5 mg/day respectively.

2. Maximum Permissible Intakes

The joint FAO/WHO Expert Committee on Food Additives has set a limit of 0.5 mg/kg body weight (7.5 mg/day for a child; 35 mg/day for an adult) as an acceptable maximum daily intake for copper.

In the development of a drinking water criteria for copper, the US EPA (1985), has focused on various human studies which suggest that ingestion of between 5.3 and 32 mg of copper/person resulted in gastrointestinal disorders, vomiting, nausea and diarrhea. Because no lasting adverse effects were reported and the symptoms could be the result of local gastrointestinal irritation, the single oral dose of 5.3 mg was considered as a lowest observed adverse effect level (LOAEL). In determining an ADI for copper, a safety factor of 2 was applied to this LOAEL, yielding a value of 2.65 mg/day. This data was also used to calculate a lifetime adjusted ADI, as the acute effects appear to be the effects of concern from exposure to copper.

Human Exposure Assessment

Humans can be exposed to chemicals such as copper from a variety of sources including drinking water, food, ambient air, soil/dusts, occupational settings and consumer products. In order to assess the health significance of copper exposure via a particular route it is necessary to assess total exposure from all routes and compare this against a permissable daily intake. In this case drinking water, air, food and soil/dusts are considered as these are sources common to all individuals. Dermal intakes are not quantified as these are considered not significant. Skin corrosion is not anticipated at the reported environmental levels.

It should be stressed that the exposure exercise in this case is tenuous because of the limited data available on environmental levels in the various media. The approach taken here is to utilize what monitoring data are available and assume that they may be representative. A complete health assessment would require comprehensive information on exposures from all sources and validation of the exposure model would require measurement of appropriate biological indicators. As with any substance, it must also be recognized that individual exposure will vary widely based on many personal choices and several other factors such as geographic location, work, diet, age, sex and health status. Individuals living in the same neighbourhood or household can experience vastly different exposure patterns. The estimates given must be viewed in light of these provisions.

A. Concentrations and Intakes from Individual Sources

1. Soils and Dusts

Exposure to copper in soils can occur via direct ingestion of soil. Soils can also serve as a source of contamination of dusts, as the uppermost layer of soil is subject to re-entrainment by wind and physical disturbance.

The average soil and dust intake for young children (1- 6 years) is estimated to be 80 mg/day. For all other age groups, an intake of 20 mg/day is assumed. From the 1988 - 89 data on copper concentrations in the 0-5 cm layer in soil the following statistics were determined:

- average concentration : 306 ug/g (n=93)
- minimum concentration : 21 ug/g
- maximum concentration : 10000 ug/g

The average was based on 0-5 cm samples only, however the values represent the range on concentrations encountered in all sample points. The maximum concentration represents only one site. The next highest level is 1800 ppm (ug/g).

Using the intake assumption and concentrations the estimated intake of copper for children is:

- average: 24.3 ug/day
- minimum: 1.7 ug/day
- maximum: 800 ug/day

The estimated intake for adults is:

- average: 6.1 ug/day
- minimum: 0.4 ug/day
- maximum: 200 ug/day

In addition to direct ingestion of soil/dusts, soil copper may possibly contribute to total intake through the dietary pathway, as root and leafy vegetables grown in such soil may contain copper residues.

Dermal exposure to copper is not estimated here. Dermal absorption is negligible through intact skin and therefore this pathway is unlikely to be a significant.

2. Drinking Water

The drinking water concentration selected (1.5 ug/L) is the mean of values for treated tap water (Decew Falls effluent) from 5/87 to 5/89 as provided by MOE Welland District Office. Data from consumer taps in the area where soil surveys were conducted were not available. Because this is measured data from the vicinity in question it is utilized in the exposure estimate. It should however also be considered that consumer tap water may contain more copper than the original water supply because of the dissolution of copper from copper piping, which is common in residential housing. The most relevant data of this type comes from a integrated monitoring survey of consumed tapwater in Ontario (MOE, 1989). The average concentration of copper in water over a one week sampling period was 176 ug/L.

3. Air

The air concentration of .15 ug/m^3 is the average of data measured from two hi-vol samplers in the vicinity of Burnstein Casting between Nov/86 and May/87. (MOE, 1987).

4. Food

a. General

Dietary copper is generally the primary source for copper exposure. No figures specific to Ontario were found that would provide an estimated intake for this media. Average dietary intakes as determined by the U.S. Food and Drug Administration for 1980 were assumed (Peninngton et, 1984 as cited in U.S.EPA, 1985). Use of these figure also assumes no consumption of foods grown on site.

b. Homegrown garden produce

It is not possible to provide a definitive statement as to the potential intake of copper from fruits and vegetables which may be grown in residential gardens in the vicinity of the site. The levels of copper in/on these plants will be a function of both foliar deposition and uptake from soil. The rate and extent of plant uptake of copper is also influenced by the type of produce, length of growing season, and soil characteristics. This type of analysis would therefore require direct sampling data on vegetables from the site.

Modelling of this exposure route also requires assumptions for estimating the consumption of homegrown garden produce. The amounts and types of produce that people might consume from a backyard garden is influenced by the size of the garden, the yields of the crop grown, and the preferences of the receptors.
The actual dose received will also be subject to reductions of concentrations in produce that result during food preparation such as washing, peeling and boiling.

According to the produce module of the AERIS (Aid for Evaluating the Redevelopment of Industrial Sites) Model for exposure, the yields of various types of crops generally range from 0.3 to 2.6 kg/m^3. For a mixture of crops as might be found in a backyard garden, a yield of 1.4 kg/m^3 has been recommended, although it is possible to achieve higher yields using special techniques and/or extraordinary effort. The model assumes that a receptors' garden is 30 m^3 @ a yield of 1.4 kg/m^3 gives a total of 42 kg, which it is indicated represents 13% of the vegetables and fruits that a one adult and one child would consume in one year.If one assumes a family size of 4, then approximately 7 % of fruits and vegetables would be garden grown.

Nutrition Canada Survey (1972) data for Ontario indicate average daily consumption of fruits, fruit products, and vegetables combined as 372 g/day (26% of total diet) for young children (1-4) and 489 g/day (32 % of total diet) for adult males, which convert to 136 kg/year and 178.5 kg/year. Assuming consumption of these vegetables through the course of the year, average daily consumption of homegrown produce would be 26 g/day for children (1.8 % of diet), 34 g/day for adults (2.2 % of diet).

Vegetable sampling on residential properties in the survey area in 1989 revealed highest copper levels in Swiss chard foliage at 10 ppm dry weight (MOE, 1990). Applying the various produce intake assumptions above and assuming 90% water content for the vegetables, yields an intake estimate of 26 ug/day copper for children and 34 ug/day for adults.

B. Estimated Intakes - Integration of Exposures

The integrated exposure estimates and assumptions employed for typical adults and children are described in Table 1. This exposure model provides crude estimates of possible copper intakes from various media in the vicinity of the Burnstein castings site. The very limited data on water and air concentrations limit the value of these estimates . Also the value assumed for food on the basis of Food and Drug Administration studies of U.S diets, does not necessarily hold for Ontario. The estimated intakes suggest that dietary copper is by far the largest contribution to total daily intake. The estimated intake from soil/dusts are 0.024 mg/day for young children and 0.006mg/day for adults, based upon the average soil copper concentrations, and represent a relatively minor contribution to total intake. The relative contribution of each pathway to total exposure is shown in Table 2.

The total estimated intakes do not include a contribution from consumption of homegrown produce as the reliability of those "estimates" is considered low. The postulated values do not significantly add to the total intake estimates.

Table 1. Integrated Exposure Estimates for Copper

Substrate or Media	Young Children (1-6 years old)	Adults
SOIL/DUSTS		
Average concentration in soil	306 ug/g	306 ug/g
Soil/Dust ingested	80 mg/day	20 mg/day
Estimated Intake via soil	24 ug/day	6 ug/day
AIR		
Concentration of Copper in Air	.15 ug/m^3	.15 ug/m^3
Volume inhaled	5 m^3/day	22 m^3/day
Estimated Inhaled copper intake	0.75 ug/day	3.3 ug/day
DRINKING WATER		
Treated tap water concentration	1.5 ug/L	1.5 ug/L
Daily water consumption	0.6L	1.5 L
Estimated Intake of copper from drinking water	0.9 ug/day	2.5 ug/day
FOOD		
Average intake of copper in U.S. toddler and adult male diets in 1980 (USEPA, 1985)	680 ug/day	1600 ug/day
ESTIMATED TOTAL DAILY INTAKE	705.9 ug or.7 mg/day per child	1612 ug or 1.6 mg/day per adult

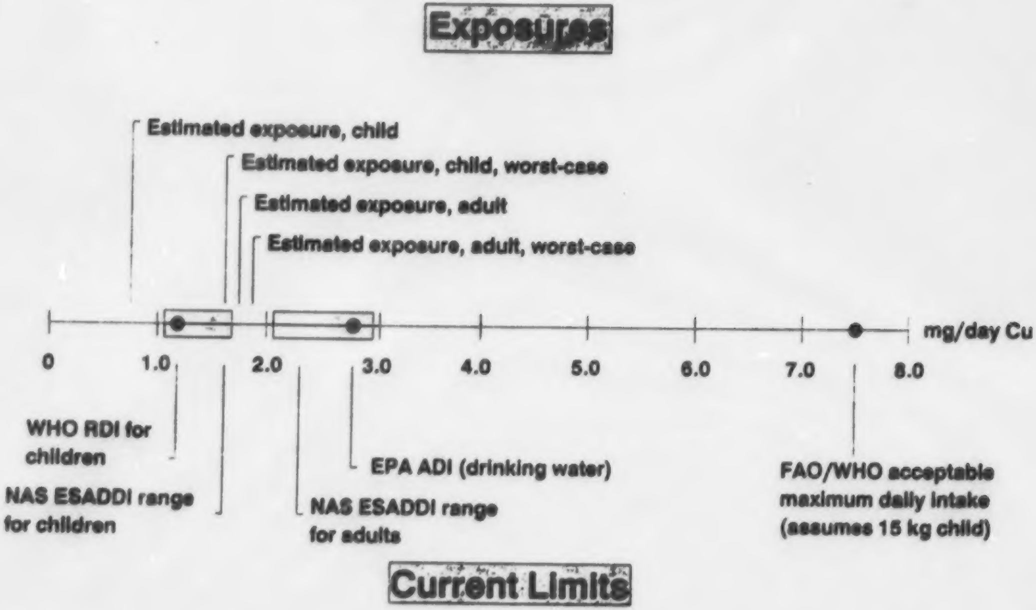
Table 2. Relative Contributions of Exposure Pathways

Substrate or Media	Child (% Total)	Adult (% Total)
Soil/Dusts	3.5	0.4
Air	0.1	0.2
Drinking water	0.1	0.2
Food	99.2	96.3

FIGURE 2:

RISK CHARACTERIZATION

(EXPOSURE AND CURRENT LIMITS FOR Cu)



Risk Characterization

In order to characterize the potential risks associated with copper contamination of soil for this community, the age-specific exposure determinations are compared to current acceptable exposure limits for this substance (see Figure 1). The estimated total exposures (0.7 mg/day/child; 1.6 mg/day/adult), utilizing copper intake from average soil levels, fall below the NAS ESADDI ranges of 1.0 - 1.5 mg/day for children and 2.0 - 3.0 mg/day for adults, the FAO/WHO acceptable maximum daily intake of 0.5 mg/kg/day (7.5 mg/day for a 15 kg child) and the ADI value of 2.65 mg/day suggested by the 1985 EPA Drinking Water Criteria document. As a worst case, if the highest soil copper concentration reported (10,000 ppm) was used in the calculations, estimated intakes of copper via direct ingestion of soil/dusts would be .8 mg/day for children and 0.2 mg/day for adults, yielding total intakes of 1.48 mg and 1.8 mg/day respectively. These worst case values are also below or within the range of acceptable intakes.

Another way to express this information is as a numerical ratio of the total exposure estimates to a reference dose (relative risk ratio, RRR = exposure / RfD or RsD. Utilizing the upper limit of the NAS ESADDI ranges for children and adults yields RRR values of 0.46 and .53 respectively. Soil/dust ingestion intakes alone would yield RRR of 1.6 X $^{10-2}$ (child) and 2.0 X 10^{-3} (adult).

The copper levels in soil in this community were estimated to result in exposures which are below currently recommended maximum acceptable health limits. These are not predicted to pose any appreciable risk to area populations based upon the small contribution of soil/dust to total exposure (3.5 % , child and less than 1% for adults) and the total multimedia exposure not exceeding current exposure limits.

Other Considerations

The approach outlined above is currently being applied to other Ontario soil monitoring data. The analysis is limited in that it does not model indoor/outdoor exposure or take into account seasonal variability. In the case described this may tend to overestimate exposures. Particular areas of uncertainty are the soil ingestion value utilized, the drinking water concentration and the general food value applied. The estimates given are deterministic and in cases where this simple analysis points to possible risks of concern, some probabilistic calculations would be developed. It is felt that these simplistic exposure estimates facilitate communication and interpretation to decision-makers and lay audiences.

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F4

A FUGACITY MODEL OF CHEMICAL FATE IN AN UNCERTAIN MULTIMEDIA ENVIRONMENT

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ABSTRACT

A modelling framework is described for estimating prevailing concentrations of chemicals in a regional multimedia environment consisting of four primary compartments, namely air, water, soil and sediment. Each primary compartment is assumed to consist of various proportions of mineral, organic, water, air and biotic phases. A common fugacity applies within, but not between, each primary compartment, although adjustment for non-equilibrium effects such as food chain biomagnification can be included. Steady state fugacities (and hence concentrations and amounts) are calculated from a knowledge of the chemical input rates and the chemical's partitioning and reactivity properties. Intermedia transport rates are expressed in terms 15 area-specific "transport velocities" which are common to all chemicals and describe processes such as evaporation, deposition and run-off.

The model can be used in conjunction with the "Linear Additivity Principle" to assign "blame" for the prevailing concentrations throughout the system to various sources of chemical.

An uncertainty analysis is included of two types. First, by incrementally adjusting the desired input terms, the sensitivity of the results (e.g. concentrations and amounts) to each input term or parameter can be assessed. This shows which parameters are most critical, i.e. to which parameters the results are most sensitive. Second, by inputting perceived confidence limits to each parameter, and running the program repeatedly with a random but limited variation in each paramater, the overall confidence limits applicable to the results can be assessed.

It is hoped that as more data become available for chemical discharge rates and multimedia concentrations, the model can be more reliably calibrated and used to assess multimedia fate and ecosystem exposure.

INTRODUCTION

There has been a significant recent increase in public concern about environmental contamination by chemicals such as pesticides and solvents. The growing public intolerance to situations in which there are even low concentrations of chemicals in air, food and water is leading to regulatory initiatives to reduce discharge rates to air, water, soil and sewers, and to eliminate the manufacture or import of certain critical persistent and toxic chemicals. Initiatives such as MISA and CAP in Ontario have this thrust.

A major problem in implementing such initiatives is that it is often difficult to identify how source reductions of say 75% removal of a chemical in a water effluent, will eventually translate into a reduction in concentrations in water or fish. Will the reduction also be 75% or will it be only 5%? The reason for this uncertainty is that most chemicals experience multimedia transport, thus for example most of the PCB in Lake Superior is deposited from the atmosphere, thus reductions of PCB quantities in direct discharges to Lake Superior will have little effect on concentrations of PCBs in water or fish. In contrast, discharges of trichloroethylene (TCE) to the aquatic environment generally have little effect on aquatic biota because most of the TCE evaporates to the atmosphere. It is thus necessary to maintain a multi-media perspective on chemical behaviour and build up the capability of deducing likely concentrations in all media as a result of discharges to a specific medium. The beneficial effects of reducing each input can then be explored and the most effective and economic measures can be implemented first. It is believed that the lack of this "cause-effect" link is a major impediment to implementation of practical measures to reduce levels of contamination, in for example, the Great Lakes Basin. When the political system is presented with a clear problem and a clear pragmatic solution it can respond appropriately. The reduction of phosphorus loadings to Lake Erie was an example. But when it has a fuzzy problem such as excessively contaminated fish and no clear set of pragmatic solutions, it fails to respond because it can not justify the cost and inconvenience. The system needs "decision support" in the form of clear statements of cause, effect and benefit, or chemical source and destination.

Regrettably, at present there is no thoroughly validated model of multi-media chemical fate in a regional environment such as Ontario, although some models have been developed and they are continually being improved. It is expected that within ten years a comprehensive multi-media modelling capability will be in place for regions such as Southern Ontario. The principal purpose of this paper is to describe recent developments in this context.

Setting of standards or guidelines should also take place in a multimedia context. The impact of an allowable concentration in one media, for example water, on other media such as air, soil, vegetation, sediment and biota should be considered. The effect on aquatic biota can be approximated from the bioconcentration factor (BCF) and persistence, and is often a determining factor in water guideline or standard setting. However, the amount that will impact air and/or other media is often not considered. For example, in the case of a persistent chemical with a high Henry's constant, the water to air partitioning could result in unacceptable air concentrations.

REGIONAL FUGACITY MODEL

Recently, our group has developed a multi-media model for the Southern Ontario Region exploiting the convenience of the fugacity approach (Mackay and Paterson 1990). For non-volatile chemicals such as metals, a similar "aquivalence" approach can be employed (Mackay and Diamond 1989).

Briefly, fugacity f Pa is used as a surrogate for concentration C mol/m^3 using the proportionality constant Z which is a function of the chemicals' properties and those of the "dissolving" medium, i.e. C is Zf. When a chemical is present in two phases or media at equilibrium, its fugacity is equal in both phases, just as chemical potential is equal. This formalism facilitates multi-media partitioning calculations by replacing partition coefficients by Z values.

Transport and transformation rates are expressed by D values, such that the rate is Df mol/h. D values which have units of mol/Pa.h contain a variety of parameters such as areas, flow rates, mass transfer coefficients, diffusivities and reaction rate constants. Of particular importance are the inter-media transport D values, e.g. for transport from air to water. The overall inter-media D value may contain several contributing parallel processes such as wet and dry deposition and adsorption. Also important are D values for reaction or degradation and advective loss for processes such as removal of chemical from a region by outflow in air or water, or burial in sediment. A full account of this approach can be found in Mackay and Paterson (1982, 1990).

In summary, all equilibrium partitioning characteristics are expressed as Z values (which are thermodynamic quantities), and all transport and transformation processes as D values (which contain Z values) and are kinetic quantities.

MEDIA

As a result of recent work, it has become clear that there is a compelling incentive to reduce the number of media (and hence the number and complexity of the mass balance equations) to a minimum. We believe that four are necessary and generally sufficient, namely air, water, terrestrial soil and aquatic sediment. Although the model treats these four primary compartments as homogeneous media when undertaking multi-media calculations, it is accepted that they consist of several contributing subcompartments such as water, suspended matter and biota. It is assumed that a common fugacity (i.e. equilibrium) prevails for chemical present in the various subcompartments of a medium. This reduces the number of fugacities in the system to four and enables the various subcompartment concentrations to be deduced from the various Z values. An overall or bulk Z value is deduced for each of the four media consisting of an appropriately volume fraction weighted total of the subcompartment values.

The key subcompartment phases are air, water, solid inorganic matter, solid organic matter (i.e. "organic carbon"), vegetable matter and animal matter. Of course, not all of these phases are present in each medium, but it is convenient to compile a table or matrix of volume fractions in each medium. It is only recently that the importance of terrestrial vegetation as a medium of transport and accumulation has been fully appreciated, so many earlier models have neglected this subcompartment. As a result of research (funded by the Ontario Ministry of Environment) we have been able for the first time to estimate Z values for various vegetation phases and include them in the model. This is important not only because of the potential of vegetation to absorb large quantities of chemical from the atmosphere and soils, but it is a critical vector in calculations of subsequent food chain exposure to domestic animals, humans and wildlife.

This issue of partitioning into vegetation has been under active investigation in our group and has been the subject of several recent reports, notably Paterson and Mackay (1989, 1990). A four compartment (root, stem, inner leaf and cuticle) plant model, illustrated in Figure 1, has been assembled. As in the environmental model, these bulk compartments are considered to consist of subcompartments of varying amounts of air, water and organic matter. Equifugacity is assumed to exist within but not between each bulk compartment. Expressions for Z values have been developed for the various compartments. Transport through the plant is described in terms of D values calculated from transport rates in the transpiration stream or xylem, and in the phloem; diffusivities in the cuticle; and mass transfer coefficients through the stomata. Metabolism in the plant and dilution by growth are also incorporated as D values. The model has been applied illustratively to a soybean plant for several organochlorines. An unsteady state version of the model has also been constructed which incorporates a simple, approximate algebraic solution which estimates the extent of approach to steady state. Validation of the model is in progress.

Table 1 is a matrix of relevant volumes and properties of the various media, the region in question being Southern Ontario.

It transpires that the key Z values used to calculate the various subcompartment and primary media Z values are for the chemical in air, water, octanol (as a surrogate or descriptor for lipids and organic carbon) and for aerosol particles. Biotic Z values are estimated from proportions of water and lipid or octanol values.

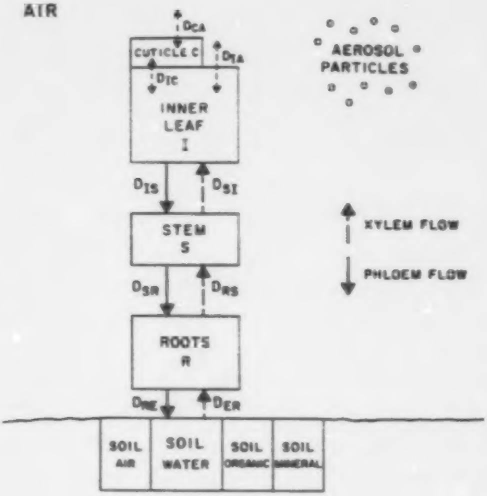
AIR
D_{CA}
CUTICLE C
D_{IA}
D_{IC}
INNER LEAF
I
AEROSOL PARTICLES
D_{IS}
D_{SI}
STEM
S
XYLEM FLOW
PHLOEM FLOW
D_{SR}
D_{RS}
ROOTS
R
D_{RE}
D_{ER}
SOIL AIR
SOIL WATER
SOIL ORGANIC
SOIL MINERAL

Figure 1. Schematic Illustration of Plant Model.

Table 1. Tentative Media Volumes and Properties.

	Primary Compartment			
	Air (1)	Water (2)	Soil (3)	Sediment (4)
Total Volume m^3	4×10^{14}	4×10^{12}	1.2×10^{10}	8×10^{8}
Horizontal area m^2	20×10^{10}	8×10^{10}	12×10^{10}	8×10^{10}
Depth m	2000	50	0.1	0.01
Bulk Density kg/m^3	1.19	1000	1500	1500
Volume fractions				
Air	1	0	0.2	0
Water	0	1.0	0.25	0.3
Inorganic Solids	2×10^{-11}	4×10^{-6}	0.43	0.65
Organic Solids	0	1×10^{-6}	0.02	0.05
Vegetation	0	1×10^{-6}	0.10	0
Animal	0	1×10^{-6}	0.001	0.001

For the purposes of calculating densities the following subcompartment densities are used: air 1.19, water 1000, inorganic solids 2500, organic solids 1000, vegetation 1000, animal 1000 kg/m^3.

Organic carbon content is 58% of organic solids content.
K_{OC} (organic-carbon-water) is 0.41 K_{OW}.

For biotic phases an effective lipid content (equivalent to octanol) of 1% in vegetation and 5% in animals.

Following this approach the volumes and "partitioning capacities" of all media can be deduced for subsequent use in the mass balance calculations.

MASS BALANCES

Mass balances can now be written for each medium including inter-media transport rates, and if the chemical input discharge and advective flow terms are known the equations can be solved to give the prevailing fugacities in each medium. Concentrations and amounts can then be deduced followed by inter-media transport rates. If desired the equations can be written in differential or unsteady state form and solved appropriately to give the time-response of the system.

The overall scheme is illustrated in Figure 2 in which the various D values are identified. Figure 3 is an example of such a calculation showing all transport rates for PCBs at steady state. A complete "chemical behaviour profile" emerges showing the relative importance of each process. An overall environmental residence time or persistence can be deduced.

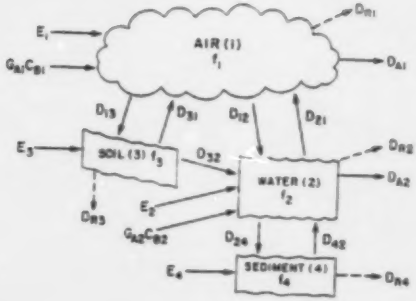

Figure 2. Environmental model illustrating transfer and transformation processes.

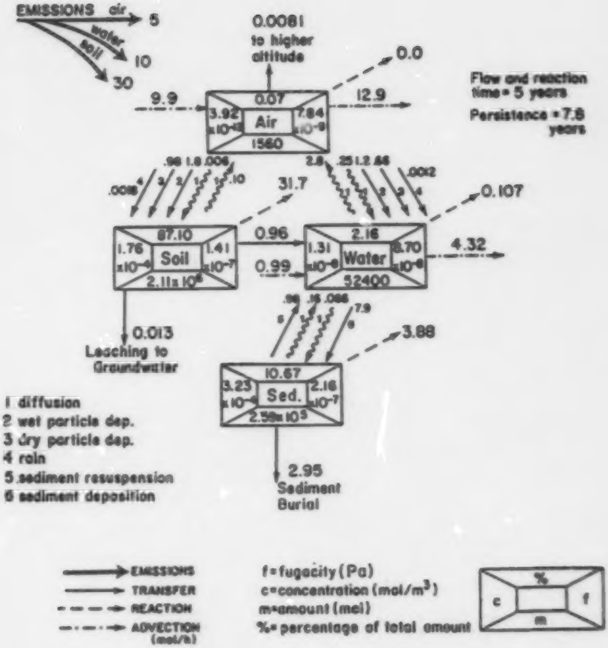
EMISSIONS
air
water
soil
5
10
30
0.0081
to higher altitude
0.0
Flow and reaction time = 5 years
Persistence = 7.6 years
9.9
12.9
0.07
3.92 x10-12
Air
7.84 x10-9
1560
.96 1.8 .006
.0018
4
3
2
1
1
.10
2.8
.25 1.2 .66
.0012
1
1
2
2
4
31.7
0.107
87.10
1.76 x10-4
Soil
1.41 x10-7
2.11x10^6
0.96
0.99
2.16
1.31 x10-6
Water
8.70 x10-8
52400
4.32
.96 .15 .066
7.9
5
1
1
6
0.013
Leaching to Groundwater
3.88
10.67
3.23 x10-4
Sed.
2.16 x10-7
2.58x10^5
2.95
Sediment Burial
1 diffusion
2 wet particle dep.
3 dry particle dep.
4 rain
5 sediment resuspension
6 sediment deposition
EMISSIONS
TRANSFER
REACTION
ADVECTION (mol/h)
f = fugacity (Pa)
c = concentration (mol/m³)
m = amount (mol)
% = percentage of total amount
%
c
f
m

Figure 3. Illustrative mass balance for PCBs.

FOOD CHAIN BIOMAGNIFICATION

A concern with the assumption of equi-fugacity in water is that there is underestimating of concentrations at high trophic levels, because of the biomagnification effect. This can be accommodated by including a simple factor such as 10 to describe this phenomenon, recognizing that this factor is dependent on the chemical's hydrophobicity. As a result of recent work on the biomagnification phenomenon (Clark et al. 1990) we believe that the effect is best described by a factor corresponding to the ratio of organism and food fugacities as calculated from the various physiological parameters such as rates of gill ventilation flow, feeding, growth and metabolism.

This effect is important from the viewpoint of exposure, but because of the small volume of biota, it is insignificant from the viewpoint of the mass balance.

This approach can be applied to biota in the terrestrial and sediment compartments.

MODEL APPLICATIONS

There are three applications of this model which we address in this discussion.

1. Attributing concentrations to sources: the linear additivity principle.

Recently Stiver and Mackay (1989) have discussed the linear additivity principle (LAP), or concept of linear superposition, as it applies to environmental calculations of this type. The principle asserts that if a contaminant's partitioning, transport and transformation processes in a multi-media environment can be expressed exclusively as linear functions of contaminant concentration (as is the case here), then the net contaminant behaviour resulting from multiple discharges in space or time is simply the sum of the behaviour resulting from each discharge individually. The principle is based on the property inherent in a linear system, that individual contaminant discharges behave entirely independently of one another in space and time, i.e. there is no interaction between contaminant discharged at one location and time, with discharges at other locations and times. At first, this assumption seems counter-intuitive because the rates of transformation and transport depend on total concentrations or gradients in total concentrations. However, as Stiver and Mackay (1989) have demonstrated, fluxes, concentrations and amounts comprise simple linear additions of contributions from individual sources.

The application in this case is to demonstrate how concentrations in the various subcompartments comprise contributions attributable to various sources, i.e. "blame" can be assigned that, for example the concentration in fish is mainly due to discharges to water and is relatively unaffected by discharges to air. This is best illustrated by an example, in this case PCBs.

There are usually five chemical input terms, direct discharges to air, water and soil and advective inflow in air and water. These are listed in Table 2, the relative proportions being obvious. The model is run for each input individually, then for all inputs simultaneously and the fugacities and concentrations noted as in Table 2. It is obvious from the linear nature of the equations that Columns 1 to 5 must add to give Column 6. This is an elementary application of the LAP. It is possible that monitoring data may be available, as in Column 7. If the model equations and parameters and the chemical input rates are correct, any discrepancy between Column 6 and 7 must be attributable to the unsteady state nature of the actual system. For example, in this case the sediments and soil are apparently more contaminated than the steady state values, presumably because of past higher discharge rates. This difference shown in Column 8 is an 'unsteady state" contribution and will (according to the model) decay to zero over a period corresponding to several residence times. It is useful to know how this level of contamination compares with the steady state level because it answers the question "Have we implemented enough controls to ensure long term satisfactory levels in say 10 years, or do we have to do more now? The model can also be used in differential form to identify the response time of the system.

Table 2. Application of the Linear Additivity Principle to the Multimedia Models.

Inputs mol/h	1	2	3	4	5	6	7	8
Discharge to air	5	0	0	0	0	5	-	-
Discharge to water	0	10	0	0	0	10	-	-
discharge to soil	0	0	30	0	0	30	-	-
Advection in air	0	0	0	9.9	0	9.9	-	-
Advection in water	0	0	0	0	0.99	0.99	-	-
Fugacities (nPa)								
Air	2.3	0.90	0.12	4.5	0.09	7.9	~8	~0.2
Water	3.9	63.5	5.8	7.7	6.3	87.2	~90	~3
Soil	3.4	1.4	130	6.8	0.13	141.7	?	?
Sediment	9.6	158	14.3	19.1	15.6	216.6	~400	~184

It is believed that this application of the LAP to multi-media models can be invaluable as a "decision support" mechanism, that is by clearly demonstrating what is accomplished by various remedial activities.

2. Environmental transport velocities.

A difficulty with this and other multi-media models is that there is a large number (possibly 50) of contributing parameters such as volumes, areas, organic carbon contents, flowrates and mass transfer coefficients. The value of each one can be questioned and the sceptical user is rightly concerned that the cumulative effect of having 50 adjustable parameters in a model is that any data can be fitted. Many of the paramaters such as volumes are determined from independent sources, but for many others an element of judgement is necessary in the selection process. In the existing model, a wide variety of environmental data has been exploited to select these values, but there is a possibility that some parameter estimates contain serious error.

An alternative approach would be (in theory) to gather discharge and media concentration data for a number of chemicals, then fit the best values of the 50 parameters to this data set. This is presently impossible because of lack of data and it would probably present severe statistical problems.

Another intermediate, less ambitious approach is to reduce the number of adjustable parameters to a minimum, estimate "typical or reasonable" values, but allow these values to vary within "reasonable" limits and try to fit the available data within these limits. This is a much more constrained and practical task. Accordingly we have devoted considerable effort in recent months to identfying the minimum number of adjustable parameters for describing inter-media process rates.

Examination of the various inter-media transport D values shows that they consist of (or can be rearranged to consist of) a combination of three types of terms. First is the inter-media area A m^2 which is defined by the dimensions of the environmental system and is available accurately. Second are Z values for the various phases in which transport occurs such as air, water and particles. These are defined by the various partition coefficients, which in turn may be estimated from the relevant physical chemical properties and quantities such as organic carbon contents and Z_V for vegetation. Finally, there are 15 transport parameters, all with dimensions of velocity (m/h) which are multiplied by Z values and areas in various combinations to give the D values, i.e. D is VAZ. These transport velocities are mass transfer coefficients, flows per unit area or ratios of diffusivity to path length. The entire transport characteristics of the system are thus defined by these 15 "transport velocities" which can be regarded as adjustable or "fittable" constants and which, to a first approximation, are independent of the chemical, although they do contain diffusion rates which are somewhat chemical-dependent. The chemical-to-chemical variability of diffusivity is, however, negligible when compared with the Z value variability.

Table 3 is a list of these "transport velocities" with our current estimates of values. Also given are "confidence limit factors" which essentially correspond to two standard deviations of a lognormal distribution, i.e. in 96% of the cases the value is expected to lie within a range of values of the parameter multiplied and divided by this factor. It is hoped that as more data becomes available these ranges can be reduced and more definitive values established. Some values such as rain rate are well known, others such as air-stratosphere transfer are relatively unimportant because other parallel processes are faster, thus the problem is not as severe as first appears. Perhaps of most concern is that these are annual average values and thus contain seasonal variations of questionable impact and magnitude. The temperature-averaging problem is particularly difficult.

Table 3. Suggested Transport Velocities and 95% Confidence limit factors (CLF). Values are rounded off to two significant figures.

	m/h	m/year	CLF
air-side air-water MTC	3	26000	3
water-side MTC	0.03	260	4
rain rate	$9.7x10^{-5}$	0.85	1.5
aerosol deposition	$6.0x10^{-10}$	$5.3x10^{-6}$	2
air diffusion in soil	0.015	130	3
water diffusion in soil	$5.8x10^{-6}$	.051	3
soil boundary layer MTC	1.0	8800	2
water-sediment diffusion	$4.7x10^{-4}$	4.1	3
sediment deposition	$4.6x10^{-8}$	0.0004	3
sediment resuspension	$1.1x10^{-8}$	0.0001	4
soil water run off	$3.9x10^{-5}$	0.34	2
soil solids run off	$2.3x10^{-8}$	0.0002	2
sediment burial	$3.4x10^{-8}$	0.0003	4
air-stratosphere transfer	0.010	90	2
soil-groundwater transfer	$3.9x10^{-5}$	0.34	2

3. Sensitivity analysis.

Examination of the results of testing this model for a number of chemicals shows that while all 15 velocities influence the fate of a chemical, they do so to very different extents depending on the chemical properties. For example, benzene evaporation is controlled by the water side mass transfer coefficient and sediment deposition rate is unimportant. For pyrene evaporation is controlled by the air-side coefficient and deposition is important. It follows that different chemicals are differently sensitive to variation in these and other parameters such as vapour pressure or organic carbon content.

To address this issue systematically we have modified the program to adjust (as desired) each parameter incrementally (by 1 %), then recalculate the fate and document the corresponding incremental change in selected output variables. The most sensitive parameters can thus be identified. Interestingly, certain values of chemical and environmental properties are often relatively unimportant (i.e. the results are insensitive), but it is not intuitively obvious which parameters control environmental fate. The corollary to this is that data for a chemical can only be used to determine environmental parameter values such as transport velocities when sufficient sensitivity exists for the parameter to affect the fate significantly. Benzene data can not be used to estimate sediment deposition rates.

From a mathematical viewpoint this process is essentially determination of the partial derivative of the result with respect to the parameter.

MONTE CARLO ANALYSIS

A recurring problem in models of this type is the question: how accurate are the results? The modeller has an obligation to convey an impression of confidence limits. This is most conveniently done by a Monte Carlo Analysis. The approach which we have adopted is to allow all the specified input parameters to vary randomly between defined confidence intervals and calculate a large number of outputs in terms of fugacities or concentrations. These outputs are averaged, distributions established, and limits determined. The outcome is a statement that the output quantity will be an average of say 6 units, but in 95% of the cases it will vary between 4 and 9 units, thus conveying a reliable impression of confidence.

To identify the sources of this variability, the sensitivity results presented earlier can be investigated to determine the most likely candidates. If desired, these sensitivities (or partial derivatives) can be weighted according to the perceived variance in the input parameters to estimate each contribution to the total variance using standard statistical error progagation equations. This enables the "blame" for uncertainty in the results to be assigned to the various input terms. If desired, more effort can then be devoted to obtaining more reliable values of the critical terms to improve the overall accuracy of the prediction.

CONCLUSIONS

In this paper we have reviewed the status of our current attempt to develop multi-media environmental models using the fugacity concept. It is believed that these models will play an increasingly useful role in aiding society to "virtually eliminate" many of these chemicals from our ecosystem. They can be used to document the link between controllable sources and ecosystem concentrations and even exposures and effects, thus identifying and justifying remedial regulatory actions. They can be used to "assign blame" to past and present discharges. It is important, however, to recognise that the models are only approximations of a very complex reality, thus it is essential to establish and convey an impression of reliability or confidence. Current efforts to accomplish this have been described. It is hoped that this will enhance the status of models as "decision support systems" and thus contribute to the purposeful elimination of contamination.

ACKNOWLEDGEMENT

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P5

POLLUTANT INTERACTIONS IN MUTAGENICITY TESTING.

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Abstract:

Many agencies test pollutant chemicals as part of their efforts to identify potential biological risks and establish guidlines for use. Natural environments of course contain many chemicals which may interact in unpredictable ways. Thus the actual hazard to plants or animals may be significantly different from that extrapolated from tests of each component alone.

An early model of promutagen interactions in short term assays suggested competition for S9 activation to explain the "less than additive" response when two chemicals were tested together. Viewed from this perspective test systems are multi-enzyme systems and may be amenable to analysis by techniques developed to handle multiple enzyme interactions. In such systems the extent of each pairwise interaction must be assessed. The overall activity is then calculated in a function which aggregates all such interactions.

We have tested nine common airborne pollutants in Ames and Micronucleus assays to develop principles of interaction [benzo(a)pyrene, 7,12-dimethylbenz(a)anthracene, 1-nitropyrene, dibenz(a,h)anthracene, benzo(b)fluoranthene, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, carbon tetrachloride and methylene chloride].

Promutagens when tested together show negative cooperativity. In such cases the surviving activity (within limits) is a linear function of log [B]/[A] where [B] and [A] are the concentration of promutagens B and A. The actual response is of the form:

$$\text{Response } [A+B] = [\text{Response A} + \text{Response B}]\, K_{AB}\, [1 - \log [B]/[A]\ ]$$

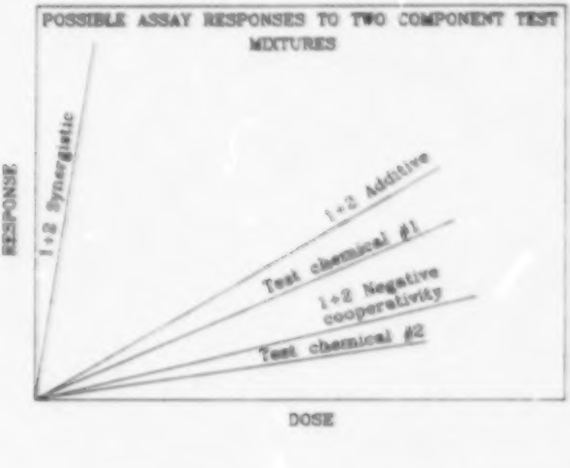
Thus for each pair of interacting chemicals an interaction coefficient K_{AB} can be determined. [Note that such coefficients are assay specific]. Interaction coefficients can then be used to predict the response in more complex mixtures (ie. more components) using a formula of the form:

Surviving activity (Risk) = [Sum of pairwise survivals] [Substrate availability]

By such an approach we have successfully predicted the activity of several multi component mixtures. Further extrapolation of this technique should allow risk assessment on real, ie. natural, atmospheres.

Introduction

In recent years an extensive literature has accumulated on the effects of individual atmospheric pollutants in various bioassays. In most instances the intention of such assays is to determine what, if any, biohazard is posed by the pollutant. Natural atmospheres of course usually contain several pollutants which may interact in various ways. Thus it would be extremely useful if the data obtained with individual chemicals could be combined in some way to anticipate the effect(s) of complex mixtures. The experience of many researchers however is that the effects of individual chemicals are rarely additive and may range from highly competitive (negative cooperativity) to highly synergistic (positive cooperativity) (Fig. 1). Further, chemicals which are themselves inactive in a particular assay may influence the assay response to another chemical. Thus the prediction of assay response due to mixtures has been elusive.



Our approach derives from a paper (1) in which negative cooperativity was assumed to be due to competition for S9, the enzymatic activating system. If the author's interpretation is correct then such systems are really multi-enzyme systems and the resulting kinetics should be amenable to analysis by the same techniques used for multi-enzyme systems (2). We have tested this approach using nine atmospheric pollutants in two bioassay systems and believe the technique can be used to anticipate the biological response to mixtures of different compositions.

MATERIALS AND METHODS

Chemicals: All chemicals were obtained from Sigma Chemical Co., Aldrich Chemical Co., Chem Service or CTC organic. In each case the highest purity available was used. S9 (a mixture of arochlor induced enzymes) was obtained from the British Columbia Research Institute.

Bacterial Strains: Histidine auxotrophs of *Salmonella typhimurium* strains TA 98 (frame shift mutant), and TA 100 (substitution deletion strain) were obtained from Professor B. Ames.

Mice: $B6C3F_1$ male mice, were purchased from Harlan Sprague Dawley Inc. The mice were used at 8-9 weeks of age.

Ames' Salmonella assay: The procedure described by Maron and Ames (3) was followed. The "Plate incorporation test" was used for mutagenicity testing. All the mutagens were tested with and without S9. If the solvent control value was within normal range, a test chemical or mixture that produced a positive dose response over three concentrations, with the highest increase equal to at least twice the solvent control value for TA 98 and TA 100, was considered mutagenic.

In vivo bone marrow micronucleus assay: This assay measures chromosomal breakage in bone marrow cells. The Assay procedure used was that of Heddle and Salamone (4) which is a modification of the original procedure of Schmid (5)

Results:

Individual Chemicals

The assay responses to each of the nine test chemicals are shown in Table 1.

Table 1

MUTAGENICITY OF INDIVIDUAL TEST CHEMICALS

Chemical	Ames Assay				MN Assay
	S9	TA 98	TA 100	Action	
1 Nitropyrene	–	+	+	Direct Mutagen	–
DMBA	+	+	+	Promutagen	+
BaP	+	+	+	Promutagen	+
Dibenz(a.h) anthracene	+	+	+	Pormutagen	+
Benzo(b) fluoranthene	+	–	+	Promutagen	+
1.1.1-tri-chloroethane	+	–	–	Non mutagen	+
1.1.2.2-tetra chloroethane	+	–	–	Non mutagen	–
Carbon tetrachloride	+	–	–	Non mutagen	–
Methylene chloride	–	+	+	Direct Mutagen	–

In the Ames Assay 1-Nitropyrene and Methylene chloride are direct acting mutagens while the remaining compounds are promutagens (S9 requiring) or non-mutagenic. In the micronucleus assay all of the promutagens (in the Ames Assay) are mutagenic as is 1.1.1-trichloroethane while neither of the directed acting mutagens (Ames Assay) is mutagenic.

Chemical Combinations:

A variety of pairwise combinations were tested in both assay systems and the data are shown in Tables 2 (Ames Assay) and 3 (Micronucleus Assay).

Table 2

MUTAGENICITY OF CHEMICAL COMBINATIONS

Ames Assay

Chemicals	Assay Response		
	S9	TA 98	TA 100
1NP + DMBA	±	S	S
1NP + BaP	±	S	S
DMBA + BaP	+	NC	NC
BaP + Dibenz (a,h) anthracene	+	NC	NC
Dibenz (a,h) anthracene + Benzo (b) fluoranthene	+	NC	NC
Dibenz (a,h) anthracene + 1,1,1 trichloroethane	+	NC	NC
Benzo (b) fluoranthene + 1,1,1 trichloroethane	+	NM	NM
1,1,2,2 tetrachloroethane + methylene chloride	+	NC	NC
Carbon tetrachloride + methylene chloride	+	NC	NC

S = Synergistic (greater than additive) Response

NC = Negative Cooperativity (less than additive)

NM = Non Mutagenic

Table 3

MUTAGENICITY OF CHEMICAL COMBINATIONS

Micronucleus Assay

Chemicals	Assay Response
1NP + DMBA	Negative Cooperativity
1NP + BaP	Negative Cooperativity
DMBA + BaP	Negative Cooperativity
DMBA + DBA	Negative Cooperativity
BaP + Dibenz (a,h) anthracene	Negative Cooperativity
Dibenz (a,h) anthracene + Benzo (b) fluoranthene	Negative Cooperativity
Benzo (b) fluoranthene + 1,1,1 trichloroethane	Non-Mutagenic
1,1,1 trichloroethane + 1,1,2,2 tetrachloroethane	Non-Mutagenic
Carbon tetrachloride + methylene chloride	Non-Mutagenic

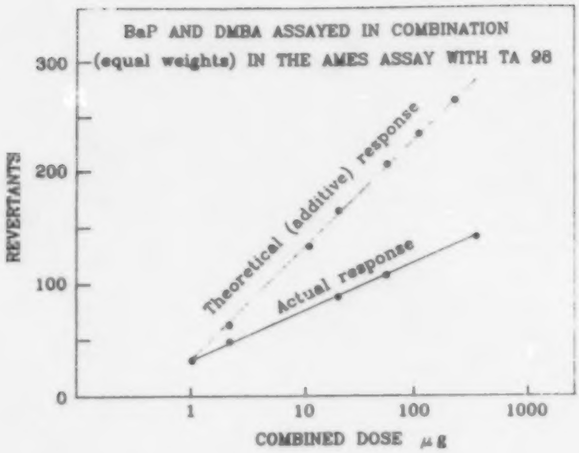
In the Ames Assay combinations involving 1NP (a direct acting mutagen) give a synergistic response. All other responses show negative cooperativity. In the case of Benzo(a)fluoranthene plus 1,1,1-trichloroethane the mutagenicity due to the former is essentially lost when combined with non-mutagenic 1,1,1-trichloroethane.

In the Micronucleus Assay all combinations were either non-mutagenic or showed negative cooperativity.

For further study of pairwise interactions we chose BaP and DMBA in the Ames Assay.

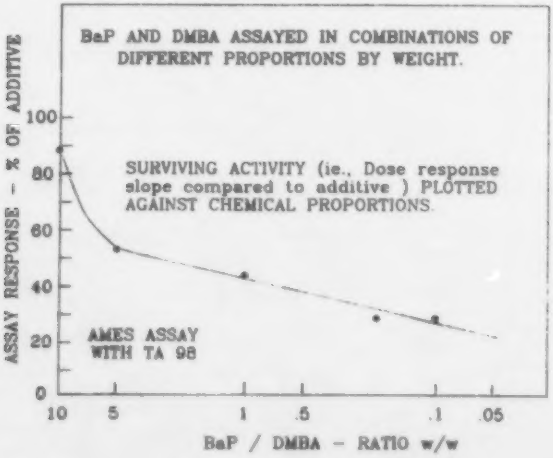
Benzo(a)pyrene and 7,12 Dimethylbenz(a)anthracene combined.

BaP and DMBA are both promutagens which, in the presence of S9, give positive responses in the Ames Assay with TA98. Standard dose response curves can be prepared for each and the anticipated response for any dose calculated. When the chemicals are tested together (with surplus S9) an additive (theoretical) response can be calculated and compared to the actual response. An example is given below.



BaP and DMBA combined in different proportions

Figure 2 shows the actual response, compared to an additive (theoretical) response, seen in the Ames assay when BaP and DMBA are added in equal amounts (w/w). This experiment was repeated with differing proportions of the two chemicals and the slope of the actual response compared with the theoritical in each case. The results obtained are shown below (Figure 3).



The addition of DMBA even well below its threshold for activity markedly inhibits the production of revertants. When the proportion of DMBA is 1/10 that of BaP or less, the actual response closely approximates the theoretical. As DMBA is increased however the response (slope of dose response curve) falls dramatically and from DMBA/BaP = .2 onward there is a linear relationship between the assay response and the $\log_{10}$ BaP/DMBA.

PAIRWISE INTERACTIONS

The preceding figure shows that the two promutagens BaP and DMBA when tested together in the Ames Assay interact to give a predictable response. In this case the theoretical response (ie. additive) is reduced by a factor proportional to the relative concentrations of the two chemicals tested. The actual response can apparently be represented by a formula such as:

$$\text{Response }(A+B) = (\text{Response }[A] + \text{Response }[B])\ K_{AB}\ (1+\log B/A)$$

When $B = A$, $1 + \log B/A \rightarrow 1$, then K_{AB} is the fractional activity remaining.

A similar relationship appears to apply to all pairs of promutagens tested when the chemicals are present in relative concentrations of approximately 1:10 to 10:1. At concentration extremes (ie. > 100:1) K increases towards the value of 1 ie. the response of a single chemical.

For each Promutagen pair an interaction constant K_{AB} can be determined which is assay specific.

	K_{AB}	
Chemical Pair	Ames	MN
BAP + DMBA	.46	.29
DMBA + DBA	NT	.12
DBA + BF	.90	.35
DBA + 1.1.1 trichloroethane	.27	.26
BaP + DBA	.57	.20
BF + 1.1.1 trichloroethane	NM	.52

Complex Mixtures

Natural atmospheres contain many chemicals with varying proportions of each. An obvious question therefore is whether pairwise interactions can be used to predict the biological response to more complex mixtures. To begin to answer this we have tested a three component mixture of BaP, DMBA and DBA (7.5/1.5/1.0. w/w/w) in the micronucleus assay. The KAB's in this case are 0.29(BaP+DMBA), 0.12(DMBA+DBA) and 0.20(BaP+DBA) and the surviving activities if each pairwise combination was tested individually would be $KAB[1 + \log {}^{B}/A]$ ie. 49%, 13% and 37% respectively.

Addition of the individual pairwise survivals would of course give a higher net surviving activity than would be expected since it does not correct for the "competition" between individual pairs for free molecules in multi-component mixtures.

ie. Net Survival = [Pairwise Survivals] [Correlation for availability]

Availability should be calculated on a molar rather than weight basis. But if as a first approximation

$$\text{Availability} = \frac{Ci}{Ci-j}$$

where Ci is the overall concentration of each component and Ci-j is the difference in concentration between components ie. free component.

Then for BaP/DMBA/DBA Surviving Activity would be predicted to be:

$$[49+13+37]\left[\frac{10}{[11.5]}\right] = 86\%$$

The actual survival was 86%

Observations and Conclusions

If assay variables, other than the concentrations of test chemicals, are carefully controlled, the interactions between pairs of chemicals in both Ames and Micronucleus assays is reproducible and predictable. Some features of such interactions include:

1) In cases where promutagens interact, the most common response is negative cooperativity;

2) The interaction between such promutagens depends on their relative proprotions and can be predicted mathematically;

3) Non-mutagens may interact with promutagens in a manner similar to another promutagen i.e. modelling ofmixtures must include the contribution (interactions) of non-mutagens;

4) In the absence of S9 some promutagens will still inhibit the action of a direct acting mutagen in the Ames assay.

These interactions while reproducible in a single assay system demonstrate some of the more general problems of risk assessment of complex mixtures. Such problems include: mutagenicity in one assay but not another, different responses with different bacterial strains (Ames assay), the requirement for S9, etc. In addition to these technical restrictions is the more general problem of extrapolating bacterial, plant or other assay data to anticipate human risk.

In spite of these difficulties risk assessment involving complex mixtures may be more reacily achievable than might be predicted. The risk due to individual chemicals an be assessed and their pairwise interactions in an animal test system can be quantitatively measured. The interaction constants thus derived may then be used in the same say as multi-enzyme systems are handled to predict the net effect of several mutagens in mixtures of different proportions.

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F6

GENOTOXIC COMPOUNDS ASSOCIATED WITH RESPIRABLE URBAN AIR PARTICULATE. CHEMICAL FRACTIONATION AND BIOASSAY OF COMPLEX MIXTURES.

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INTRODUCTION:

The composition of mixtures of polycyclic aromatic compounds (PAC) found in association with respirable particulate in an urban air environment is dependent on season, atmospheric condition, industrial activity, motor vehicle traffic, residential density and many other variables (1-3). Some of the compounds associated with urban air particulate are toxic or carcinogenic and could have an adverse effect on human health (4,5). Characterization the impact of human activities on environmental health requires the marriage of analytical chemistry and genetic toxicology (the study of chemical or physical activities which pose a mutagenic or carcinogenic risk). Rigorous chemical analyses of organics associated with urban air particulate has provided valuable information about the types and classes of PAC in the environment (6-8). Genotoxicology, on the other hand, has produced new and additional insight into the problems associated with exposures to the complex mixtures of extractable organic compounds from air particulate and the risks such exposures pose to humans (7). While not all known chemical carcinogens are detected by all or, indeed in some cases, any of the STTs, these tests provide the most rapid method of screening for genotoxicity.

Nearly three thousand chemicals have been identified in the earth's atmosphere (6). The chemical analysis of organic extracts of total suspended respirable particulate has been extensively reported (9,10). While initial concerns have been directed at the investigation of the unsubstituted polycyclic aromatic hydrocarbons (PAH), these do not by any means account for all the genotoxic biological activity in environmental samples (11). Complex mixtures extracted from air particulate contain substituted PAH (alkyl, amino, chloro, cyano, hydroxy, oxy or thio groups) as well as heterocyclic derivatives of PAH (7).

The use of biological assays for genotoxic activity in total extractable organic material from urban air particulate has been used to examine the relation between mutagenicity associated with air particulate and a number of factors including seasonal weather patterns, geography, vehicle traffic and industrial development (2). Nishioka *et al.* (12) identified hydroxynitrofluorenone, an hydroxylated and nitrated derivative of pyrene, isomers of hydroxylated nitromethylfluorenone hydroxylated nitro-derivatives of benzene, toluene, naphthalene, and biphenyl in the fractions of a massive air sample which contained significant mutagenic activity.

The objective of this research is to examine polycyclic aromatic hydrocarbons (PAH) and PAH derivatives adsorbed to respirable urban particulate ($< 10\ \mu m$) and to assess the health hazard they present. A class-selective chemical fractionation procedure coupled with an analysis by a combination of chromatographic methods and short term tests (SSTs) for genotoxins. We report progress in three areas: (1) chemical characterization of the fractionated material; (2) identification of fractions most active in bioassays; and (3) correlation of genotoxicity of specific fractions in bacteria with the corresponding activity for DNA adduct production in mammalian cells.

MATERIALS AND METHODS:

Air particulate samples (selected for respirable particulate with aerodynamic diameter <10 μm) were collected for 24h periods using a PM10 sampler (General Metal Works) with flow controller set at 40 ft^3/min (1630 m^3/24h). All suspended particulate samples were collected on Teflon/glass fibre filters (Pallflex 8 x 10 inch type TX40H120WW). One sampler was sited at Toronto (Station # 31104) on Bredalbane St., and at two locations in Hamilton: Downtown on the roof of an OME station #29000 at the intersections of Kelly and Elgin Streets, and Westdale (Station # 29118) at the intersection of Main St West and the exit of Highway 403). Typical values for 24h samples are given in Table 1. Actual mean diameter of particulate collected was 0.105 μm (range 0.013 to 0.46 μm).

Table 1: COMPARISON OF PM10 RESPIRABLE PARTICULATE BY LOCATION

Average Load: (24h, 40cfm)	Maximum	Minimum
HAMILTON		
Downtown (Kelly and Elgin)	0.089844g (0.0526)[1]	0.326600 (0.0193)
Westdale (Main St. West)	0.062679g (0.0329)	0.146700 (0.0176)
TORONTO (Bredalbane)	0.049340g (0.0303)	0.166450 (0.0115)

[1] Standard deviation N= 85

Sample loadings of respirable particulate varied with the site (Table 1). On average Westdale, received seventy percent of the total respirable particulate that was measured at the downtown site on the same days. At the Downtown location where both PM10 and hi-vol units were located, the respirable particulate averaged 62% of the total suspended particulate (0.144223g (.0814) N= 83). Toronto sample values averaged somewhat lower than those from Hamilton (79% of Westdale). An important difference between the values for the two cities was that the Toronto sampler was sited more than 12m above street level, while Hamilton samplers were located at less than 4m.

PARTICULATE EXTRACTION METHODS:

Filters collected for a designated period or atmospheric condition were pooled and Soxhlet extracted successively with dichloromethane (DCM) and methanol (MEOH) for 16h. The organic extract was fractionated according a scheme shown in Figure 1. The organic extract was loaded onto a neutral alumina column and sequentially eluted with solvents of increasing strength yielding the following fractions: [A1] (hexane), [A2] (benzene), [A3] ($CHCl_3$/ 1% methanol), [A4] (methanol), [A5] (methanol/water) and [A6] (water). Fractions [A2] and [A3] as well as [A4] and [A5] were pooled to yield fractions [A23] and [A45]. Aliphatics which were a major contaminant in [A23] were removed by chromatography on Sephadex LH20.

Alumina fractions [A23/LH20] and [A45] were subjected to further separation using gradient normal phase and/or gradient reverse phase HPLC. For these tasks a Hewlett Packard 1090 chromatograph equipped with diode array and fluorescence (Kratos) detectors and a HP Chem-Station was used. Preparation of subfractions of alumina fraction [A23LH20] are described. Normal Phase HPLC Conditions: 250 x 9.4 mm i.d. 10 m Whatman Magnum-9 PAC column, maintained at 35°C. **Solvent gradient:** as a percent of dichloromethane (CH_2Cl_2) in hexane at different times; 0% from 0-5 min, 1% at 10 min, 5% at 15 min, 100% at 40 min and then isocratic at 100% CH_2Cl_2 until 50 min. At 50 min a second gradient was initiated from 100% CH_2Cl_2 to 100% absolute ethanol over 10 min then held for 5 min at 100% ethanol. **Flow rate:** 4.2 mL/min. Reverse Phase HPLC conditions: Two 250 x 4.6 mm i.d. 10 m Vydac 201TP104 columns connected in series, maintained at 40°C. **Solvent gradient**(linear): 60% to 100% acetonitrile in water over 30 minutes, then hold at 100% acetonitrile. **Flow rate:** 1.0 mL/min. Details of NPLC or RPLC of fraction [A45] are given in the figure legends.

BACTERIAL ASSAYS:

The *Salmonella typhimurium*/microsome assays for mutagenic activity with or without Araclor 1254 induced rat liver S9 (4%) were performed as described by Maron and Ames (13). Tester strains were supplied by B.N. Ames (TA98) or M. Watanabe (TA1538/DNP[pYG122]).

RESULTS:

Table 2 shows the mutagenic activity found in the crude alumina fractions from the pooled Spring, 1989 filters. Mutagenic activity, expressed as revertants per m^3 air, was determined from dose response curves (five doses, duplicate assays). Virtually all detectable mutagens were divided between the two pooled eluent fractions [A23] and [A45]. All mutagenic activity was recovered after the passage of [A23] through Sephadex LH20 (a step used to remove non-mutagenic aliphatics). Both **DIRECT AND INDIRECT** acting mutagens (-/+ S9) were about equally divided between these two fractions [A23LH20]: 43.5%; [A45]: 42.7% without S9; [A23LH20]: 49.9%; [A45]: 43% in the presence of S9 microsomal activation.

Fraction [A23LH20] typically contains 50-60% of mutagens detected by the *Salmonella*/microsome assay. The alumina fraction (free of aliphatics) was further fractionated by normal phase chromatography (NPLC) into seven [N] fractions. Results for mutagenicity expressed as revertants per cubic meter are given in Table 3. These values were calculated from linear regression for dose response curves based on five dilutions done in duplicate. Values for a minimum of two doses must exceed 2X background to be considered positive.

TABLE 2: *MUTAGENICITY VALUES FOR ALUMINA FRACTIONS: 1989*

DATE	REVERTANTS PER M^3 OF AIR FRACTION [A1]	[A23/LH20]	[A45]	[A6]
Spring: 1989				
TA98 -S9	0.47	1.58	2.0	0.17
TA98 +S9	0.20	4.50	3.88	0.13

TABLE 3: *[N] FRACTIONS FROM SPRING 1989: RECOVERY OF MUTAGENIC ACTIVITY IN TA98*

FRACTION	rev/m^3-S9	rev/m^3+S9
[N1]	0.23 (10.6)[1]	0.26 (6)
[N2]	1.04 (47.9)	2.24 (48.3)
[N3]	0.28 (12.9)	0.32 (7)
[N4]	0.34 (15.7)	0.34 (7)
[N5]	0.18 (8)	0.21 (4.5)
[N6]	0.17 (8)	0.07 (1.5)
[N7]	0.45 (20.7)	1.19 (25.6)
TOTAL[2]	2.71	4.64
MUTAGENIC ACTIVITY OF FRACTION [A23LH20][3] FROM CRUDE ALUMINA):	1.05	3.32
PERCENT RECOVERY: Σ[N1...N7]*100/[A23LH20]:	258	140

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[1] Percent of total activity recovered in the fraction.

[2] Σ[N1...N7] in revertants per cubic meter.

[3] Mutagenic activity (expressed as revertants per cubic meter) of total filter equivalents loaded onto column for normal phase chromatography.

An example of the distribution of mutagenic activity in each of these [N] fractions is given in Figure 2. Here, fractions [N1] through [N4] have been further fractionated by reverse phase chromatography (RPLC). Eluant from RPLC run was collected at thirty second intervals and each fraction tested in the *Salmonella* assay. Results are shown for activity with microsomal activation. Compounds in these fractions were identified through computer comparison of the UV spectra of peaks with those in the spectral libraries of PAC's and their derivatives.

Approximately ten percent of the mutagenic activity in [A23LH20] (5% of the total) elutes with [N1] (panel A, Figure 2), the least polar compounds form the NPLC fractionation step. Fraction [N1] of Hamilton air samples typically contain a number of PAH (Figure 3A). Quantities of these compounds vary, but they appear in every [N1] fraction of air extract regardless of wind direction or time of year. Interestingly, [N1] from filters collected in Toronto (which represent lower particulate loadings) contains additional compounds to those of Hamilton. These include triphenylene, benzo(b)naphtho-(2,1-c,d)thiophene, benzo(j)fluoranthene, benzo(a)pyrene, benzo(b)chrysene, benzo(e)pyrene, picene, and anthanthrene (see Figure 3B).

Soxhlet extraction of urban air particulate is preferred over sonication in organic solvent. Quantitative analysis of our extraction protocol using a NBS Standard Reference Material, SRM 1649 (urban dust/organics). The NBS method of extraction was optimized to yield PAH. In the [N1] fraction of the Urban Dust 1649 extract we identified: perylene, fluoranthene, pyrene, triphenylene, benz(a)anthracene, chrysene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, picene, and coronene. Quantitative analysis for four compounds detected pyrene, 1.01 g/g, triphenylene, 0.812 g/g, chrysene, 1.13 g/g, and benzo(a)pyrene, 1.09 g/g, out of an original 0.980g sample of particulate. With the exception of pyrene, these values represent a yield of approximately 50% of the values determined by NBS. The values were determined from UV spectra rather than fluorescence which is the more sensitive technique. This, and the fact that the chromatography was not optimized for PAH separation may be an explanation for the variation from NBS values.

Figure 2 shows quite clearly that most of the PAC which show activity in the bioassay system are found in fractions other than [N1] which contains most of the readily identified PAH. Small amounts of individual fractions collected during the RPLC of [N2] were subjected to further analysis. Gas chromatography and gas chromatography\mass spectrometry of specific [R] fractions produced a number of potential identifications. The rise and fall of the total ion current as components exited the column. This was compared to the rise and fall of the mutagenicity in the mutachromatogram. Identities of potential mutagens were ascertained. Analysis of the mass spectral data, resulted in proposal of six structures for nine potential mutagens found in one subfraction [R] of the [N2] fraction and these are presented in see Figure 4. The specific [R] fractions were found to contain ketonic, nitrated, halogenated, and alkylated aromatic hydrocarbons. Two possible structure determinations were a chlorinated quinone and phenanthrene derivative, based of the mass spectral data.

DISCUSSION:

The results presented confirm and extend previous results. Previous reports have examined the influence of ozone, $NO+NO_2$ and wind direction on the relative abundance of mutagens detectable by the bacterial assay system. We have used additional, more sensitive strains of bacteria which contained larger amounts of nitroreductase and *N/O*-acetyltransferase which apparently greatly increased the sensitivity of the bioassay system. These strains possess increased ability to metabolise and activate nitro-PAH or PAH derivatives that are acetylated or activated to N-acetoxy intermediates. TA98, relative to the other two strains consistently gives the weakest response to a given fraction. Addition of the plasmid pKM101 to these strains has yet again produced a substantial rise in sensitivity of the bioassay (data not shown). This is an indication that a significant portion of the detectable mutagens in atmospheric particulate samples could be nitro-PAH or their derivatives.

The apparent elevated levels of nitro-PAH detected by the bioassay system implicates NO and NO_2 as important actors in the genotoxicity of urban air particulate. Further chemical analysis will clarify which components of the atmospheric emissions provide the greatest concern for human health. The fractions discussed here as well as the more polar [A45] are capable of producing significant numbers of DNA adducts in rabbit tracheal epithelial cells (results not shown). Concentrated research on the identities of the mutagens, the DNA adducts and the mutations they produce in mammalian cells is being carried out in our laboratories.

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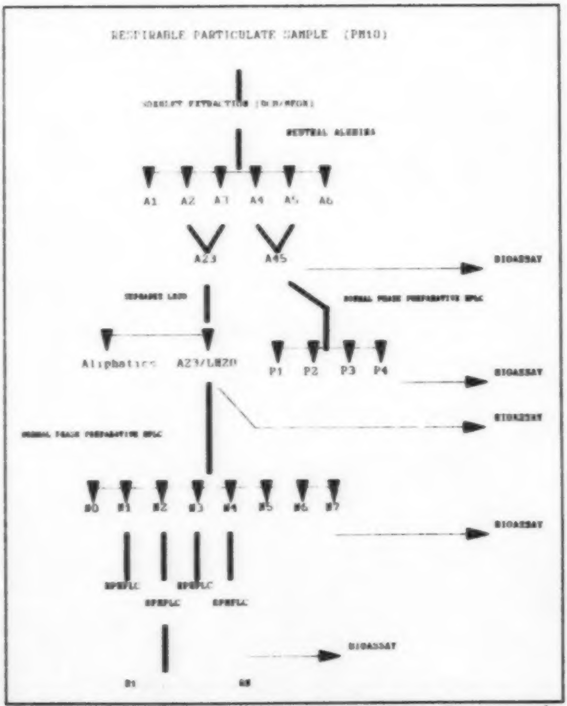

RESPIRABLE PARTICULATE SAMPLE (PM10)
SOXHLET EXTRACTION (DCM/MEOH)
NEUTRAL ALUMINA
A1
A2
A3
A4
A5
A6
A23
A45
BIOASSAY
SEPHADEX LH20
NORMAL PHASE PREPARATIVE HPLC
Aliphatics
A23/LH20
P1
P2
P3
P4
BIOASSAY
BIOASSAY
NORMAL PHASE PREPARATIVE HPLC
N0
N1
N2
N3
N4
N5
N6
N7
BIOASSAY
RPHPLC
RPHPLC
RPHPLC
RPHPLC
BIOASSAY
R1
RN

Figure 1: Overall fractionation scheme for organic extract of respirable air particulate.

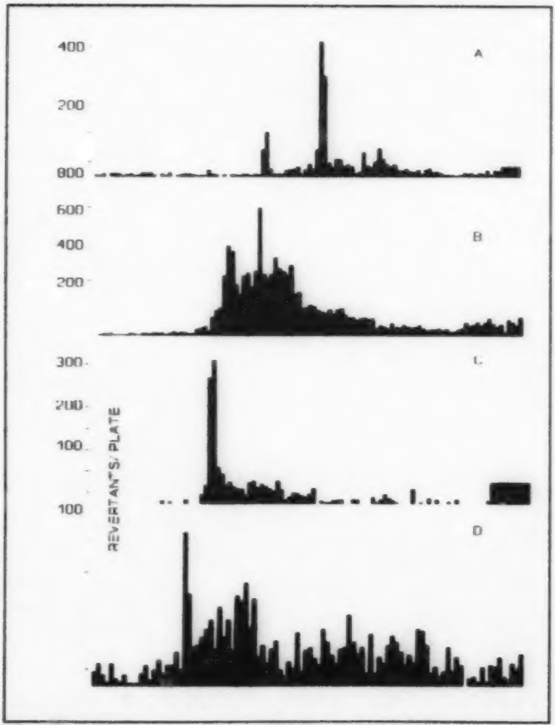


Figure 2:Reverse phase HPLC mutachromatograms of [N] fractions. An example of how mutagenic activity is distributed in [A23/LH20] using *Salmonella* strain TA1538/DNP9(pYG122) with S9 activation.

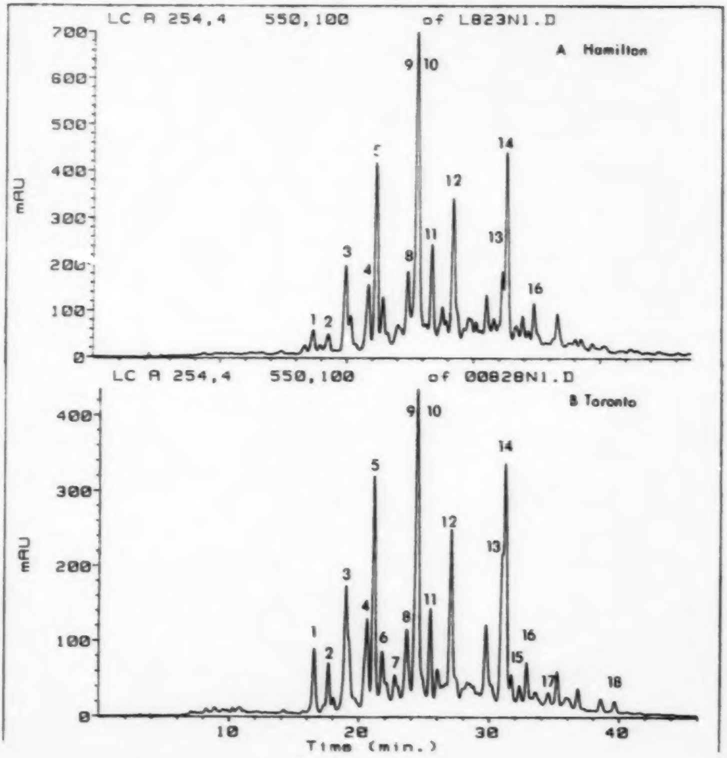
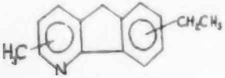
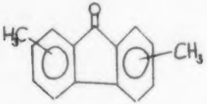


Figure 3: Reverse Phase Chromatography of [N1] fractions from (A) Hamilton air particulate, or (B) Toronto air particulate. The absorbance profiles at 254 nm are shown although spectral information was acquired between 240 and 550nm.

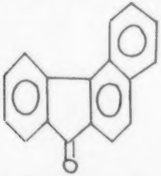
(1) Fluoranthene
(2) Pyrene
(3) Benzo[b]fluorene
(4) Benzo[a]anthracene
(5) Chrysene
(6) Triphenylene
(7) Benzo[b]naptho[2,1-c,d]thiophene
(8) Benzo[j]fluoranthene
(9) Benzo[e]pyrene
(10) Benzo[b]fluoranthene
(11) Benzo[k]fluoranthene
(12) Benzo[a]pyrene
(13) Benzo[ghi]perylene
(14) Indeno[1,2,3,-cd]pyrene
(15) Benzo[b]chrysene
(16) Picene
(17) Anthanthrene
(18) Coronene



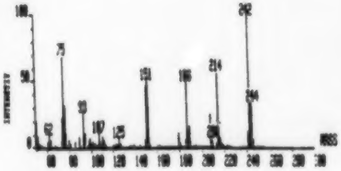
The structure for the compound which eluted at scan number 367 in fraction 19.

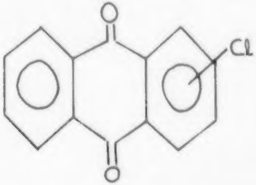


The structure for the compound which eluted at scan number 590 in fraction 19.

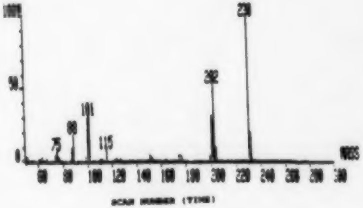


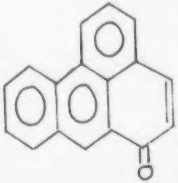
The structure for the compound which eluted at scan number 728 in fraction 30.





The mass spectrum for scan number 437 in fraction 20. The below structure is for a compound which may be causing the indirect mutagenic activity.





The mass spectrum for scan number 499 in fraction 20. The structure below is of a possible mutagen which may be causing the indirect mutagenic activity.

Figure 4: Structures of possible mutagenic compounds isolated from [N2].

F7

Ministry Research Needs in Biotechnology

by
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Introduction

The Ministry of the Environment has only recently become involved in biotechnology, which can be defined as the application living organisms or their products and by-products to provide goods and services. As many applications of biotechnology will involve the introduction of novel organisms directly into the environment, concerns have been raised regarding the risks to human health and the environment which may be associated with such introductions. Regulations are being developed in various jurisdictions to ensure that the risks associated with biotechnology products are assessed prior to their environmental introduction. A major component of these regulations is the development of scientifically founded approaches for assessing the risks in the area of biotechnology. To gain a better understanding of factors which need to be considered when assessing novel organisms prior to their environmental introduction, the Ministry has identified several key issues related to biotechnology risk assessment as potential areas in which to sponsor innovative research. These issues include: the development of detection and monitoring methods, the investigation of gene transfer phenomena, contingency planning, and general microbial ecology.

The Ministry also recognizes that many applications of biotechnology can provide significant social and economic benefits. These can result from reducing our dependence on traditional chemicals and through the development and exploitation of organisms designed to metabolize toxic compounds *in situ*. The Ministry has therefore identified the environmental applications of biotechnology as an additional area in which to sponsor innovative research. For the environmental applications of biotechnology, research is needed in the areas of bioremediation, analytical methodology, and biological alternatives to chemical pest control agents.

Details of the specific research needs in each of these areas are discussed below.

Research Needed

I. Assessing the Environmental Impact of Novel Organisms

The short and long term impact that repeated applications of biotechnology products, especially novel microorganisms, might have on the environment is poorly understood. In order to gain a better understanding of the risks which may

be associated with such introductions, research is needed to understand of the biological relationships in various ecosystems and how they might be affected by the introduction of novel organisms or organisms engineered to carry novel traits.

I A. Detection and Monitoring

- Develop and evaluate sensitive methods for detecting and accurately enumerating populations of microorganisms in terrestrial and aquatic environments.

- Develop improved methods for recovering and analyzing DNA from environmental samples.

- Develop genetic or biochemical markers which can be used to unambiguously identify and quantify populations of novel organisms introduced into the environment.

I B. Contingency Planning

- Develop suitable protocols and methods to deal with accidental spills and releases of biotechnology products containing viable microorganisms.

I C. Gene Transfer

- Investigate and develop methods to accurately determine the degree of genetic transfer which may occur between and among, discrete populations of microorganisms.

- Investigate the environmental and genetic factors which contribute to genetic transfer between, and among, species or strains of microorganisms.

I D. Ecological Effects

- Investigate and identify natural variables which may have an impact on the population dynamics and species diversity in terrestrial or aquatic ecosystems.

- Based on the known factors which influence population dynamics and species diversity in established ecosystems, develop predictive models to estimate the potential environmental impact that novel organisms might have on a particular ecosystem.

- Investigate biological, or physical parameters for use as sensitive end points